UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

August 23, 2007

REPLY TO THE ATTENTION OF:

SR-6J

Mr. Jerry C. Winslow
Principal Environmental Engineer
Xcel Energy
414 Nicollet Mall (Ren. Sq. 8)
Minneapolis, Minnesota 55401

RE: Final Revisions to BERA,
Ashland/NSP Lakefront Superfund Site

Dear Mr. Winslow:

In accordance with the Administrative Order on Consent (AOC), CERCLA Docket No. V-W-04-C-764, Section X, Subparagraph 21(c), the United States Environmental Protection Agency (EPA) is modifying the Baseline Ecological Risk Assessment (BERA) submission to cure certain deficiencies. By letter dated December 22, 2006, EPA provided Northern States Power Company (NSPW), (d.b.a. Xcel Energy) a notice of deficiency regarding the BERA. EPA provided a second notice of deficiency on July 10, 2007, giving NSPW 21 days to cure the deficiencies by incorporating EPA's modifications. NSPW submitted the revised BERA on July 31st. EPA, in consultation with WDNR, reviewed NSPW's revised BERA. EPA has agreed to incorporate the revisions; however, on page 3-11, one modification needs to be incorporated into the BERA. Since EPA has already provided two notices of deficiency on the BERA, EPA invokes its right to modify the BERA pursuant to Subparagraph 21(c). The attached document is, therefore, the final BERA for the Ashland/NSP Lakefront Superfund Site. Please submit the attached document as the final BERA within 7 days. In addition, all supporting documents (Tables, Appendices, etc.) need to be consistent with the final BERA.

If you have any questions, please contact me at (312) 886-1999.

Sincerely,

Scott K. Hansen
Remedial Project Manager

cc: Dave Trainor, Newfields
Jamie Dunn, WDNR
Omprakash Patel, Weston Solutions, Inc.
Henry Nehls-Lowe, DHFS
Ervin Soulier, Bad River Band of the Lake Superior Chippewa
Melonee Montano, Red Cliffe Band of the Lake Superior Chippewa

FINAL REPORT

BASELINE ECOLOGICAL RISK ASSESSMENT - ASHLAND/NORTHERN STATES POWER LAKEFRONT SUPERFUND SITE

VOLUME I: MAIN REPORT

Prepared for

Northern States Power Company - WI
1414 West Hamilton Avenue
Eau Claire, WI 54701

July2007

URS
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Milwaukee, WI 53226
25688375.70000

A Baseline Ecological Risk Assessment (BERA) was conducted to describe the likelihood, nature and severity of adverse effects to ecological receptors resulting from their exposure to contaminants at the Ashland/NSP Lakefront Superfund Site (Site) under current conditions.

This BERA supports the Ashland/NSP Lakefront Superfund Site Remedial Investigation/Feasibility Study (RI/FS) being conducted under the regulatory framework of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. 9601, et seq. and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), 40 CRF Part 300. It supplements two other ecological risk assessments that have been conducted for this Site. In 1998, SEH completed an Ecological Risk Assessment (ERA) of the contaminated sediments adjacent to Kreher Park (SEH 1998). A supplemental ERA was performed in 2001 (SEH 2002) during which additional sediment toxicity testing was conducted to provide information for determining clean up goals for the sediments.

The scope of work conducted as part of the RI studies for this BERA was approved by USEPA on December 7, 2004. The approved scope of work resulted from extensive discussions with various stakeholders and Natural Resource Trustees, including:

- National Oceanographic and Atmospheric Administration (NOAA),
- Wisconsin Department of Natural Resources (WDNR),
- Red Cliff Band of Lake Superior Chippewa Indians, and
- Bad River Band of Lake Superior Chippewa Indians.

This BERA was prepared following USEPA Guidance including, *Ecological Risk Assessment for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final.* (USEPA 1997).

The Site consists of property owned by Northern States Power Company, a Wisconsin corporation [d.b.a. Xcel Energy, a subsidiary of Xcel Energy Inc. ("NSPW")], a portion of Kreher Park, and sediments in an offshore area adjacent to Kreher Park[1]. Based on current data, the impacted area of Kreher Park consists of a flat terrace adjacent to the Chequamegon Bay shoreline. The surface elevation of the park varies approximately 10 feet, from 601 feet above mean sea level (MSL), to about 610 feet above MSL at the base of the bluff overlooking the park. The bluff rises to an elevation of about 640 feet above MSL, which corresponds to the approximate elevation of the NSPW property.

The lake elevation fluctuates about two feet, from 601 to 603 feet above MSL. At the present time, the park area is predominantly grass covered. A gravel overflow parking area for the marina occupies the west end of the property, while a miniature golf facility formerly occupied the east end of the site. The former City of Ashland waste water treatment plant (WWTP) and associated structures front the bay inlet on the north side of the property. The impacted area of Kreher Park occupies approximately 13 acres and is bounded by Prentice Avenue and a jetty

[1] Reference to this portion of the Site as Kreher Park developed over the course of this project. Kreher Park consists of a swimming beach, a boat landing, an RV park and adjoining open space east of Prentice Avenue, lying to the east of the subject study area of the Site. For purposes of this report and to be consistent with past reports, the portion of the Site to the west of Prentice Avenue, east of Ellis Avenue and north of the NSPW property is referred to as the "Kreher Park Area" or simply Kreher Park.

extension of Prentice Avenue to the east, the Canadian National railroad to the south, Ellis Avenue and the marina extension of Ellis Avenue to the west, and Chequamegon Bay to the north.

The offshore area with impacted sediments is located in a small bay created by the Prentice Avenue jetty and marina extensions previously described. For the most part, contaminated sediments are confined within this small bay by the northern edge of the line between the Prentice Avenue jetty and the marina extension. The impacted sediments consist of lake bottom sand and silts, and are overlain by a layer of wood chips, likely originating from former lumbering operations. Based upon MGP operation history there is no evidence that the wood in the bay is a result of purifier box waste from the MGP. The chips layer varies in thickness from 0 to seven feet, with an average thickness of nine inches and overlay approximately 95% of the sediment that is potentially affected by contamination. Based on current data, the entire area of potentially affected sediments encompasses approximately ten acres.

As part of this RI, a number of investigations were conducted whose results were used, along with historical information, to support this BERA. All of the historical and current data were used for screening for contaminants of potential concern (COPCs). Investigations conducted during this RI to support the BERA included:

1) Surface soil samples collected in the vicinity of Kreher Park (See RI report URS 2006a);
2) Sediment samples collected as part of the supplemental sediment sampling and Sediment Quality Triad (Triad) investigations;
3) Sediment toxicity testing;
4) Benthic macroinvertebrate community studies;
5) Collection of fish tissue;
6) Surface water collection; and
7) Characterization of wetlands and terrestrial habitats..

The details of these investigations are in the reports appended to this BERA or in reports submitted separately to USEPA.

Problem Formulation

The initial step of the BERA was to screen all data, including all historical data, relating to level of Site-related contaminants against conservative generic guidelines and benchmarks for soil, sediment and surface water quality. These benchmarks included Wisconsin's Consensus-Based Sediment Quality Guidelines (WDNR 2003), USEPA Region V's Ecological Screening Levels (ESLs) and USEPA Ecological Soil Screening Levels (ECO-SSLs) as well as other similar benchmarks.

Based upon this screening a number of contaminants of concern (COPCs) were identified (Table ES-1).

Table ES-1. List of COPCs by Medium Based on Maximum Detected Concentration.

Surface Water	Sediment	Soil
None	Total polycyclic aromatic hydrocarbons (PAHs)	Total PAHs
	Dibenzofuran	Benzene
	m-Cresol	Antimony
	o-Cresol	Barium
	p-Cresol	Cadmium
	1,2,4-Trimethylbenzene	Chromium
	1,3,5-Trimethylbenzene	Copper
	Benzene	Lead
	Ethylbenzene	Manganese
	Toluene	Mercury
	Total Xylenes	Selenium
	Antimony	Silver
	Barium	Thallium*
	Cadmium	Zinc
	Copper	Cyanide
	Iron	
	Lead	
	Manganese	
	Mercury	
	Nickel	
	Selenium	
	Silver	
	Thallium	
	Vanadium	
	Zinc	
	Cyanide*	

* Eliminated as a COPC based on frequency of detection (<5%)

As part of the Problem Formulation, an overall risk management goal was developed as the basis for evaluating risk at the Site:

Maintenance (or provision) of soil, sediment and water quality as well as food source, and habitat conditions capable of supporting a "functioning ecosystem" for the aquatic and terrestrial plant and animal populations (including individuals of protected species) inhabiting or utilizing the Ashland/NSP Lakefront Superfund Site area.

Assessment endpoints were developed based upon this risk management goal.

After development of a conceptual site model describing:

- The source of contamination;
- Release and transport mechanisms;
- Contact point and exposure media;
- Routes of entry; and
- Key receptors.

Assessment endpoints, risk questions and measurement endpoints were selected as the basis for the BERA. These are summarized in the following table (Table ES-2).

Table ES-2. Endpoints and Risk Questions.

Assessment Endpoint	Risk Question	Measurement Endpoint(s) (Exposure and Effects)
Benthic macroinvertebrate community	Are concentrations of contaminants in the sediments at the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?	• Determine the concentrations of Site-related contaminants in Site sediment. • Determine the levels of soot, coal, coke and slag, which may moderate the bioavailability of PAHs in the sediment. • Determine the levels of acid volatile sulfides (AVS) and simultaneously extractable divalent metals (SEM) in the sediment. • Compare concentrations of metals measured in Site sediment to WDNR (2003) sediment quality guidelines for threshold and probable effects. • Evaluate, quantitatively or qualitatively the bioavailability of sediment associated COPCs using SEM:AVS or Equilibrium Partitioning approach. • Compare concentrations of PAHs that accumulated in worm tissues in the bioaccumulation bioassay to the No Effects Body Residue (NEBR) that is associated with narcosis caused by PAHs and volatile organic compounds (VOCs). Use this as a model for predicting risk at the Site. • Using sediment toxicity bioassays, determine which sediments at the Site have elevated toxicity to surrogates for resident macroinvertebrate species compared to sediments in reference areas. • Determine on the basis of benthic macroinvertebrate sampling and analysis where benthic communities inhabiting sediments in waterbodies in and adjacent to the Site are impaired when compared to benthic communities inhabiting reference area sediment.

Table ES-2. Endpoints and Risk Questions.		
Assessment Endpoint	**Risk Question**	**Measurement Endpoint(s) (Exposure and Effects)**
Fish community	Are concentrations of contaminants in sediments and surface waters at the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?	• Determine the concentrations of Site-related contaminants in Site surface water. • Determine the concentrations of Site-related contaminants in tissue from fish caught in and adjacent to the Site. • Compare tissue levels of PAHs and estimated VOCs in wild fish caught at the Site to the NEBR. • Using sediment bioassays, determine whether areas on and adjacent to the Site have elevated toxicity compared to sediment from reference areas to surrogates for juvenile resident fish species. • Compare the concentrations of Site-related contaminants in tissue from fish caught in and adjacent to the Site to levels in fish from reference areas. (This assessment endpoint will be used only qualitatively as an indicator of exposure).
Omnivorous aquatic bird community	Are dietary exposure levels of Site-related contaminants sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?	• Determine the concentrations of Site-related contaminants in Site sediment. • Through food chain models for the black duck using sediment to benthic invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to toxicity reference values (TRVs) associated with adverse effects, including reproductive impairment.
Omnivorous birds	Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?	• Determine the concentrations of Site-related contaminants in Site soils. • Through food chain models for the red-winged blackbird using soil to vegetation and soil to invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including

Table ES-2. Endpoints and Risk Questions.

Assessment Endpoint	Risk Question	Measurement Endpoint(s) (Exposure and Effects)
		reproductive impairment.
Insectivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous avian community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Through food chain models for the tree swallow using sediment to emergent insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Piscivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to individual ospreys or to the piscivorous avian community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Determine the concentrations of Site-related contaminants in fish caught in and adjacent to the Site. • Through food chain models for the double-crested cormorant and the osprey using actual levels of Site-related contaminants measured in fish in and adjacent to the Site, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Omnivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the omnivorous mammal community?	• Determine the concentrations of Site-related contaminants in Site soils. • Through food chain models for the white-footed mouse using soil to plant and soil to invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Table ES-2. Endpoints and Risk Questions.		
Assessment Endpoint	**Risk Question**	**Measurement Endpoint(s) (Exposure and Effects)**
Insectivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous mammal community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Through food chain models for the big brown bat using sediment to emergent insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Piscivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?	• Determine the concentrations of Site-related contaminants in fish caught in the Site area. • Through food chain models using actual levels of Site-related contaminants measured in fish, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects.

Based upon these risk questions and endpoints a number of Receptors of Concern (ROCs) were selected (Table ES-3).

Table ES-3. Receptors of Concern.

ROC Category	ROC	Habitat
Aquatic Habitat		
Benthic macroinvertebrate community	Generic	Littoral portions of Chequamegon Bay
Fish Community	Generic	Littoral portions of Chequamegon Bay
Omnivorous birds	Black Duck	Littoral portions of Chequamegon Bay
Insectivorous birds	Tree swallow	Upland and riparian
Piscivorous birds	Double-crested cormorant Osprey (State endangered)	Littoral portions of Chequamegon Bay
Insectivorous mammals	Big brown bat	Upland and riparian
Piscivorous mammals	Mink	Upland and riparian
Terrestrial Habitat		
Omnivorous birds	Red-winged blackbird	Upland and riparian
Omnivorous mammals	White-footed mouse	Upland and riparian

Effects Analysis

The Effects Analysis consisted of an evaluation of available toxicity or other effects information that could be used to relate the exposure estimates to a level of adverse effects. Stressor-response (i.e., effects) data that were used to evaluate ecological risks in this BERA were of three types: (1) literature-derived toxicity data, (2) site-specific ambient media toxicity tests (e.g. sediment toxicity tests), and (3) site-specific biological community surveys.

The focus of the majority of the effort for this BERA was on aquatic portions of the Site. For the evaluation of Site sediment, all three lines of evidence were integrated into a Sediment Quality Triad approach (Triad) (Long and Chapman 1985; Chapman et al. 1987). The Triad evaluates sediment quality by integrating spatially and temporally matched sediment chemistry, biological, and toxicological information. Benthic invertebrate community analysis and sediment toxicity testing provided site-specific information regarding potential ecological effects of exposure of ecological receptors to COPCs in the Site sediment. These additional lines of evidence supplement traditional bulk sediment chemistry data to provide a more relevant, site-specific assessment of risks.

The evaluation of bulk sediment chemistry data involved comparison of Site sediment chemistry data to effects levels published by WDNR (2003), derived from relevant studies reported in published literature, or from studies performed for this BERA. Site-specific sediment toxicity tests were conducted with aquatic receptors that are representative surrogates for those living on the Site and the results of this testing provided information on potential toxic effects that were observed in Site relevant organisms exposed to Site sediment. Site-specific surveys of benthic macroinvertebrate community also were conducted for the Site. In addition to these three lines of evidence that focus primarily on the benthic environment at the Site, surface water quality data and fish tissue data were collected from Site waters.

For upland portions of the Site, only two lines of evidence were used in this BERA. One was the comparison of bulk soil chemistry to soil quality benchmarks used as generic criteria, e.g., the soil ECO-SSLs (USEPA 2005a) or derived from relevant studies reported in published literature. The second was the comparison of doses accumulated through the food chain that terrestrial and aquatic prey-dependent wildlife (i.e., birds and mammals) may feed upon. These doses were compared to TRVs derived from the primary scientific literature.

The result of the ecological effects analysis was a range of TRVs that were compared with the dose estimates (birds and mammals) or toxicological benchmarks that were compared with *estimated exposure point concentrations* (EPCs) (benthic invertebrates and fish) to estimate potential risks in this Risk Characterization.

Exposure Analysis

In the exposure analysis, the relationship between receptors at the Site and potential stressors (chemical, biological, or physical entities that may result in adverse effects to one or more receptors or groups of receptors) were evaluated. Exposure point calculations (EPCs) used to estimate exposure were calculated as the mean and 95% upper confidence limit of the mean concentration (UCL_{95}) of the exposure medium. EPCs calculated for surface water, sediment, soil, or tissue residues were based directly upon the levels of contaminants in these media.

Exposure estimates for birds and mammals were calculated using food chain models. Simplified food chain models were developed to calculate average daily doses (ADDs) of COPCs that selected receptor groups experience through exposure to surface water, sediment, and surface soil at the Site. The ADD represents the dose of a chemical that a receptor may ingest if it foraged within designated exposure units. ADDs for wildlife receptors are calculated using (1) EPCs for prey and media developed for each, (2) COPC-specific bioaccumulation factors or bioaccumulation models for dietary items, and (3) receptor-specific exposure parameters and food chain model assumptions, (e.g., diet composition, foraging area, amount of incidental soil or sediment ingested, etc.).

Risk Characterization

Risk Characterization was the final phase of the BERA. In the Risk Characterization the information from the effects and exposure analyses was used to determine a probability of adverse effects to ROCs and discuss the strengths, weaknesses, and assumptions in the BERA. Risk estimates (or Hazard Quotients) were developed for each assessment endpoint based upon comparison of site-specific media concentrations and/or estimated ingested contaminant dose estimates (the latter for wildlife) to effects levels (generic criteria, benchmarks and TRVs) for the various ROCs. Finally risk was characterized for each assessment endpoint by integrating the risk estimate with the results of other lines of evidence, if available.

The results of the risk characterization indicated that there are potentially unacceptable impacts to the benthic macroinvertebrate community in aquatic portions of the Site. Two lines of evidence, bulk sediment chemistry and sediment toxicity testing, indicated that some impairment at the community level was possible. Effects observed from field surveys of the existing benthic community indicated effects that were less dramatic than those demonstrated in the laboratory toxicity studies, but interpretation of the field survey data is made very difficult by a high degree of variability and lack of comparability between reference and site stations.

However, the fact that hydrocarbons are sporadically released from the Site sediment during some high energy meteorological events or when disturbed by other activities indicates the potential for impact to the benthic community that may not have been fully measured by the benthic community studies conducted to support the RI. While there is no evidence that effects from these releases will lead to impairment of populations and communities of these receptors inhabiting the waters of Chequamegon Bay, it remains a source of uncertainty. It is possible that the presence of this continuing source of site related contaminants may sporadically impair the healthy functioning of the aquatic community in the Site area.

In addition, if normal lake front activities, i.e, wading, boating etc., were not presently prohibited, the disturbance of sediments and concomitant release of subsurface COPCS would increase. This potentially could lead to greater impacts than were measured during these RI/FS studies.

The BERA concludes that the potential for adverse effects to ecological receptors other than benthic macroinvertebrates was not sufficient to result in significant adverse alterations to populations and communities of these ecological receptors.

The following table (Table ES-4) summarizes the results of the BERA.

ES-4. Conclusions of the Baseline Ecological Risk Assessment.

Assessment Endpoint	Risk Question	Conclusion of BERA
Benthic macroinvertebrate community	Are concentrations of contaminants in the sediments in Chequamegon Bay adjacent to the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?	Based upon two lines of evidence (risk estimates and sediment bioassays), there are potentially unacceptable impacts to the benthic macroinvertebrate community in aquatic portions of the Site although these impacts were not documented at a community level by a focused benthic community investigation. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the benthic macroinvertebrate community is exposed to them should be addressed in the Feasibility Study.

ES-4. Conclusions of the Baseline Ecological Risk Assessment.

Assessment Endpoint	Risk Question	Conclusion of BERA
Fish community	Are concentrations of contaminants in sediments and surface waters of waterbodies in and adjacent to the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?	There is no unacceptable risk to the fish community utilizing the Site. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the fish community is exposed to them should be addressed in the Feasibility Study.
Omnivorous aquatic bird community	Are dietary exposure levels of Site-related contaminants sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?	There is no unacceptable risk to the omnivorous aquatic bird community utilizing the Site. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the omnivorous aquatic bird community is exposed to them should be addressed in the Feasibility Study.
Omnivorous birds	Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?	There is no unacceptable risk to omnivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Insectivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous avian community?	There is no unacceptable risk to insectivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Piscivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to individual ospreys or to the piscivorous avian community?	There is no unacceptable risk to piscivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Omnivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the	There is no unacceptable risk to omnivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility

ES-4. Conclusions of the Baseline Ecological Risk Assessment.		
Assessment Endpoint	**Risk Question**	**Conclusion of BERA**
	omnivorous mammal community?	Study.
Insectivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous mammal community?	There is no unacceptable risk to insectivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Piscivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?	There is no unacceptable risk to piscivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.

TABLE OF CONTENTS

Tables

Figures

Exhibits

Appendices

ACRONYMS, ABBREVIATIONS, AND DEFINITIONS[2]

µg/g	Micrograms per gram (parts per million)
µg/kg	Micrograms per kilogram (parts per billion)
µg/L	Micrograms per liter (parts per billion)
$\mu W/cm^2$	Microwatt per square centimeter
ACR	Acute to chronic ratio
ADD	Average daily dose
Ag	Silver
AH	Aromatic hydrocarbons
ANCOVA	Analysis of covariance
AOI	Area of interest
ARARs	Applicable or relevant and appropriate requirements
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
AUF	Area use factor
AVS	Acid volatile sulfides
AWQC	Ambient water quality criteria
BAF	Bioaccumulation factor
BaP	Benzo(a)pyrene
BERA	Baseline Ecological Risk Assessment
BSAF	Biota sediment accumulation factors
BTEX	Benzene, toluene, ethylbenzene, and xylene
BW	Body weight
CBR	Critical body residue
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
COC	Chemical of concern
COPC	Chemical of Potential Concern
CS	Contaminated sand
CSM	Conceptual Site Model
Cu	Copper
CW	Contaminated wood
DBH	Diameter breast height
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DQO	Data Quality Objective
ECOSAR	Ecological Structure Activity Relationships
ECO-SSL	Ecological Screening Level
EC_{20}	Effective concentration – 20 percent response
EC_{50}	Effective concentration – 50 percent response
ED_{20}	Effective dose – 20 percent response
ED_{50}	Effective dose – 50 percent response

[2] This list includes acronyms, abbreviations, and definitions used in the BERA text and appendices.

USEPA	U.S. Environmental Protection Agency
EPC	Exposure point concentration
ERA	Ecological Risk Assessment
ERAGS	Ecological Risk Assessment Guidance for Superfund
ERED	Environmental Residue Effects Database
ER-L	Effects range-low
ER-M	Effects range-median
ESA	Endangered Species Act
ESL	Ecological Screening Level
ETO	Ephemeroptera, trichoptera, odonata
FS	Feasibility Study
GPS	Global Positioning System
ha	Hectare
Hg	Mercury
HHRA	Human health risk assessment
HMW-PAHs	High molecular weight polycyclic aromatic hydrocarbons
HOMO	Highest occupied molecular orbit
HQ	Hazard Quotient
IR	Ingestion rate
Kow	Octanol-water partition coefficient
LMW-PAHs	Low molecular weight polycyclic aromatic hydrocarbons
LOAEC	Lowest observed adverse effect concentration
LOAEL	Lowest observed adverse effects level
LOEC	Lowest observed effects concentration
LSRI	Lake Superior Research Institute
LUMO	Lowest unoccupied molecular orbit
MD	Maryland
MDR	Minimum daily requirement
mg/kg	Milligrams per kilogram (parts per million)
mg/kg/d	Milligrams per kilogram per day
mg/kg BW/d	Milligrams per kilogram body weight per day
mg/L	Milligrams per Liter (parts per million)
MGP	Manufactured gas plant
MI	Michigan
MSL	Mean sea level
NA	Not applicable
NC	Not calculated
NCP	National Contingency Plan
NE	Not established
NEBR	No effect body residue
NOAA	National Oceanic and Atmospheric Administration
NOAEC	No observed adverse effect concentration
NOAEL	No observed adverse effects level
NOC-PAH	PAH concentration normalized to organic carbon
NOEC	No observed effects concentration
NOEL	No observed effects level

NRDA	Natural Resource Damage Assessment
NRWQC	National Recommended Water Quality Criteria
NSP	Northern States Power
NWI	National Wetland Inventory
OC	Organic carbon
ORNL	Oak Ridge National Laboratory
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
PCBs	Polychlorinated biphenyls
PEC	Probable effects concentration
PER	Photoenzymatic repair
POM	Particulate organic matter
ppm	Parts per million
ppb	Parts per billion
PRG	Preliminary Remedial Goal
QA	Quality assurance
QAPP	Quality assurance project plan
QSARs	Quantitative structure-activity relationships
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROC	Receptor of concern
SLERA	Screening Level Risk Assessment
SEM	Simultaneously extractable metals
SMDP	Scientific Management Decision Point
SQUIRT	NOAA Screening Quick Reference Table
SQT	Sediment Quality Triad
SVOC	Semivolatile organic compound
SW	Surface Water
T&E	Threatened and endangered
TEC	Threshold effect concentration
TEL	Threshold Effects Level
TLM	Target Lipid Model
TOC	Total organic carbon
TPAH	Total polycyclic aromatic hydrocarbons
TRV	Toxicity Reference Value
TU	Toxic unit
UCL	Upper Confidence Limit
UPL	Upper Prediction Limit
USACE	U.S. Army Corp. of Engineers
USFS	U.S. Forest Service
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
UV	Ultraviolet light
UVA	Ultraviolet light (340-400 nm)
UVB	Ultraviolet light (280-320 nm)
UVC	Ultraviolet light (200-280 nm)

VOC	Volatile organic compound
WCMP	Wisconsin Coastal Management Program
WDNR	Wisconsin Department of Natural Resources
WI	Wisconsin
WPBCO	Weathered Prudhoe Bay crude oil
WWTP	Waste water treatment plant
Zn	Zinc

1.1 OBJECTIVE AND SCOPE

The objective of this baseline ecological risk assessment (BERA) is to describe the likelihood, nature and severity of adverse effects to ecological receptors, both plants and animals, resulting from their exposure to contaminants at the Ashland/NSP Lakefront Superfund Site (Site) under current conditions.

The BERA has been prepared to support the Ashland/NSP Lakefront Superfund Site Remedial Investigation/Feasibility Study (RI/FS) being conducted under the regulatory framework of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. 9601, et seq. and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), 40 CRF Part 300.

This BERA supplements two other ecological risk assessments that have been conducted for this Site. In 1998, SEH completed an Ecological Risk Assessment (ERA) of the contaminated sediments adjacent to Kreher Park (SEH 1998). A supplemental ERA was performed in 2001 (SEH 2002) during which additional sediment toxicity testing was conducted to provide information for determining clean-up goals for the sediments.

The scope of work conducted as part of the RI studies for this BERA was approved by USEPA on December 7, 2004. The approved scope of work resulted from extensive discussions with various stakeholders and Natural Resource Trustees, including:

- National Oceanographic and Atmospheric Administration (NOAA),
- Wisconsin Department of Natural Resources (WDNR),
- Red Cliff Band of Lake Superior Chippewa Indian Tribe, and
- Bad River Band of Lake Superior Chippewa Indian Tribe.

In addition U.S. Fish and Wildlife Service reviewed the scope of work before it was implemented.

1.2 GUIDANCE

The guidance that was followed in preparation of this BERA includes:

- Ecological Risk Assessment for Superfund: Process for Designing and Conducting Ecological Risk Assessments, Interim Final. Environmental Response Team, Edison, NJ. (USEPA 1997);
- Guidance for the Data Quality Objective Process (USEPA 2000);
- Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites. OSWER Directive 9285.6-08 (USEPA 2002a); and,
- Contaminated Sediment Remediation Guidance for Hazardous Waste Sites. USEPA-540-R-05-012. OSWER 9355.0-85. (USEPA 2005b).

1.3 REPORT ORGANIZATION

The BERA is organized as follows:

Section 2.0 – Site History and Description

This section includes a description of the site and a brief summary of the historical operations.

Section 3.0 – Baseline Problem Formulation

This section includes the elements of Problem Formulation: refinement of contaminants of potential concern (COPCs); description of regional ecosystems and human communities; presentation of conceptual site models (CSM); identification of receptors of concern (ROCs); development of risk questions/hypotheses and assessment endpoints, lines of evidence and measurement endpoints.

Section 4.0 – Step 4: Study Design and Data Quality Objective Process

This section establishes the study design and data quality objectives of the BERA. In this section, the conceptual site model is completed and measurement endpoints are identified to evaluate the assessment endpoints established in Section 3.0.

Section 5.0 – Analysis

This section includes the exposure and effects analysis for the BERA.

Section 6.0 – Risk Characterization

The risk estimate and risk description are presented in this section.

Section 7.0 – Summary and Implications for Risk Management

The conclusions of he BERA are summarized in this section

Section 8.0 – References

2.1 SITE DESCRIPTION [EXCERPTED FROM THE RI/FS WORKPLAN (URS 2005)]

The Site consists of property owned by Northern States Power Company, a Wisconsin corporation (d.b.a. Xcel Energy, a subsidiary of Xcel Energy Inc. ("NSPW") a portion of Kreher Park, and sediments in an offshore area adjacent to Kreher Park. The Site is located in S 33, T 48 N, R 4W in Ashland County, Wisconsin, shown on Figure 2-1. Existing site features showing the boundary of the site are shown on Figure 2-2.

Based on current data, the impacted area of Kreher Park consists of a flat terrace adjacent to the Chequamegon Bay shoreline. The surface elevation of the park varies approximately 10 feet, from 601 feet above MSL, to about 610 feet above MSL at the base of the bluff overlooking the park. The bluff rises to an elevation of about 640 feet above MSL, which corresponds to the approximate elevation of the NSPW property. The lake elevation fluctuates about two feet, from 601 to 603 feet above MSL. At the present time, the park area is predominantly grass covered. A gravel overflow parking area for the marina occupies the west end of the property, while a miniature golf facility formerly occupied the east end of the site. The former City of Ashland waste water treatment plant (WWTP) and associated structures front the bay inlet on the north side of the property. The impacted area of Kreher Park occupies approximately 13 acres and is bounded by Prentice Avenue and a jetty extension of Prentice Avenue to the east, the Canadian National Railroad to the south, Ellis Avenue and the marina extension of Ellis Avenue to the west, and Chequamegon Bay to the north.

The offshore area with impacted sediments is located in a small bay created by the Prentice Avenue jetty and marina extensions previously described. For the most part, contaminated sediments are confined within this small bay by the northern edge of the line between the Prentice Avenue jetty and the marina extension (Figure 2-3). The affected sediments consist of lake bottom sand and silts, and are overlain by a layer of wood chips, likely originating from former lumbering operations. The chips layer varies in thickness from 0 to seven feet, with an average thickness of nine inches and overlay approximately 95% of the sediment that is impacted. Based on current data, the entire area of impacted sediments encompasses approximately ten acres.

2.2 SITE HISTORY [EXCERPTED FROM THE RI/FS WORKPLAN (URS 2005)]

Historically, Chequamegon Bay has been utilized as a vital transportation route for the shipment of various materials to and from Ashland including iron ore, lumber, pulp and coal. During the late 19th and early 20th centuries, Ashland was one of the busiest ports on the Great Lakes. In recent times, the shipping volume through the bay has declined because of the decline in the mining, smelting and lumber industries in the region.

The Kreher Park area is reclaimed land of which the south boundary defined the original lake shoreline. Beginning in the mid to late 1800's, this area was filled with a variety of materials including slab wood, concrete, demolition debris, municipal and industrial wastes and earthen fill that created the land now occupied by the park. The filled area was used for lumbering and sawmill activities which occurred during the deforestation of the northern portion of Wisconsin around the turn of the century. Timber was also cut in various places in the area, including the Apostle Islands and the Arrowhead region of Minnesota, and the logs rafted into the Ashland area where they were floated awaiting processing. The large amount of wood "mulch"[3] in aquatic portions of the Site provides testimony to the log rafting that occurred here. The extensive amount of bark mulch-sized wood particles and small wood chips found on and in the sediment today likely originated from the constant working of the logs in the log rafts as well as, perhaps, the disposal of wood debris from the saw mill operation. Based on the MGP operation there is no evidence supporting that wood in the bay is a result of purifier box waste from the MGP.

In addition to the lumbering operations, the Site area has also been used as:

- A "dump" for solid waste, fly ash, and dredge spoils by property owners, residents, and the United States Army Corps of Engineers;
- The City of Ashland Waste Water Treatment Plant;
- A manufactured gas plant; and
- Secondary wood processing plants including possible wood treatment and shingle manufacturing.

Since the mid-1980's a full service marina has also operated at the foot of Ellis Avenue.

2.3 PHYSICAL SETTING [EXCERPTED FROM THE RI/FS WORKPLAN (URS 2005)]

The Site is located at the top of a ravine on the shore of Chequamegon Bay. Regional surface water drainage flows to the north through Fish Creek and several small unnamed creeks and swales into Chequamegon Bay. Surface water at the Site flows either to the City of Ashland storm sewer system, or discharges directly to Chequamegon Bay.

Soils in the Ashland area generally consist of surficial deposits underlain by red clay and silt deposits of the Miller Creek Formation. Geology of the upper bluff area in the vicinity of the former ravine consists of earthen fill materials, with clay soils of the Miller Creek Formation on the flanks of the former ravine. The ravine fill unit consists of silty clay fill material mixed with ash, cinders, slag, and fragments of bricks, concrete, glass, wood, and other solid waste.

Offshore geology consists of a discontinuous layer of submerged wood mulch on the lake bottom underlain by variably fine to medium grained sediments. Silts and clays of the Miller Creek Formation underlie the sediments.

2.3.1 Climate

The regional climate of the Ashland area is mid-continental, being highly influenced by adjacent Lake Superior. The average daily high varies from 19.1 F° during January to 79.2 F° during July. Total annual precipitation averages nearly 33 inches. The highest precipitation levels occur during the summer months, although the total annual snowfall averages nearly 100 inches. The

[3] The term wood mulch probably best describes the conditions of most wood debris and wood waste found overlying the surface sediment. Most of it is ground up pieces or bark and twigs not unlike bark mulch. In addition to the wood mulch there is a variety of other wood waste including logs, shingles and other manufacturing wood waste, branches, and twigs.

average first frost occurs in mid-September and the average last frost does not occur until the end of May. Chequamegon Bay is generally ice-bound between December and April.

2.3.2 Population and Land Use

The population of the City of Ashland is 8,620 based on the 2000 census results. Residents are served by the city's municipal water supply, which is provided from Chequamegon Bay surface water from an area about one mile northeast of the Site.

3.1 SCOPE OF BASELINE PROBLEM FORMULATION

Problem formulation is the systematic planning process that identifies the factors to be addressed in a BERA and consists of several activities, including:

- Refinement of the preliminary list of chemicals of potential concern (COPCs) at the site [(i.e., those that were identified during the screening level ecological risk assessment (Section 3.6)];
- Development of management goals and objectives that provide an explicit statement of the desired condition of the valued entity being protected (Section 3.9);
- Identification of assessment endpoints (Section 3.11),
- Review and refinement of the information relating to the fate and transport of COPCs, potential exposure pathways, and the information on receptors potentially at risk (Sections 3.10);
- Development of a conceptual model with risk questions that the risk assessment will address (Sections 3.10);
- Identification of lines of evidence and measurement endpoints to address the risk hypotheses (Sections 3.11 and 4.1).

3.2 RESULTS OF PREVIOUS ECOLOGICAL RISK ASSESSMENTS CONDUCTED FOR THE ASHLAND/NSP LAKEFRONT SUPERFUND SITE

In 1998, SEH completed an Ecological Risk Assessment (ERA) of the contaminated sediments adjacent to Kreher Park (SEH 1998). The 1998 ERA concluded that there is evidence that some sediments at the Site were contaminated to the degree that they were harmful to benthic organisms living in them.

Several lines of evidence were used in the 1998 investigation including:

1) a literature search conducted to select relevant sediment effects benchmarks for evaluation of Site data and to identify ecological effects documented at other sites with similar contaminants and exposures;
2) sediment and surface water samples collected, analyzed, and compared to sediment and surface water effects benchmarks for the contaminants identified;
3) collection of fish for analysis of tissue chemical concentrations;
4) a limited survey conducted of the benthic community at contaminated and reference locations; and
5) a series of laboratory bioassays conducted to characterize the effects of short term exposure to contaminated and reference sediment samples.

A supplemental ERA was performed in 2001 (SEH 2002) during which additional sediment toxicity testing was conducted to provide information for determining clean-up goals for the sediments.

The following sections summarize the various lines of evidence used and the conclusions of these two preliminary ecological risk assessments.

3.2.1 Sediment and Surface Water Chemical Data Evaluation

Sediment chemical data from the Site were compared to several sets of effects levels for both dry weight units (µg/g) and normalized-to-organic-carbon (NOC) units (µg/gOC). Semi-volatile (SVOC) and volatile organic compounds (VOC) sediment benchmarks were exceeded for several chemicals at several locations in the shallow bioactive zone sediments (0-15 cm) and deeper sediments. Based on this comparison, the report concluded there was a high probability of adverse effects to aquatic life from the contaminated sediments.

No contaminants were detected in twelve unfiltered surface water samples collected on January 14 and 15, 1998. However, in one unfiltered water column sample collected during a period on May 14, 1998, when wave heights were estimated to be between 60 and 90 cm,[4] benzo(a)anthracene and benzo(a)pyrene exceeded secondary chronic and acute water quality criteria values, respectively. No VOCs exceeded water quality criteria in that sample. It is unknown whether the contaminants in this sample were adsorbed onto suspended particulates or in a dissolved state. However, it is likely they were bound to suspended particles because more water soluble PAHs that are much more abundant in the Site sediments, were not detected.

3.2.2 Fish Tissue Study

A study was conducted to evaluate levels of PAHs in fish caught at the Site and to evaluate the condition of the fish at the Site. Results from this study indicated that there was no evidence of external deformities in the fish. Of 27 fish collected on May 18, 1998, October 14, 1998 and May 28, 1999, fewer than 50% had measurable levels of any PAHs, either low molecular weight (LMW) or high molecular weight (HMW) in their tissues (Correspondence from Henry Nehls-Lowe to Jamie Dunn, et al., January 12, 2000). No fish collected had measurable amounts of high molecular weight PAHs in their tissues. The PAHs detected were low molecular weight PAHs including naphthalene, acenaphthene, anthracene, fluorene, and phenanthrene. Total PAH concentrations ranged as high as 483 µg/kg in the whole fish samples.

3.2.3 Benthic Community Evaluation

A limited benthic community survey was conducted in 1998 (SEH 1998). Four stations were sampled, two contaminated stations (one in sand, the other in wood debris) and two reference stations (one in sand, the other in wood debris) (Table 3-1). Benthic community survey results were evaluated for richness, abundance and relative indices. Graphical analyses indicated that the two contaminated stations and the reference wood station were degraded compared to the reference sand station.

[4] It is likely that estimate was based upon crest to trough height rather than wave height compared to lake surface.

Table 3-1. Benthic Community and Bioassay Stations Used in 1998 SEH Study

Total PAH Concentration	Contaminated Wood	Contaminated Sand	Reference Wood	Reference Sand
µg/g	370.2	1.5	6.5	0.4
µg PAH/g OC (NOC)	21776.5	583.6	114.8	92.2

3.2.4 Bioassays

Bioassays were conducted in 1998 on several sediment samples collected from the same two contaminated wood and sand stations and two reference wood and sand stations (SEH 1998). These were the same two stations where the benthic community samples were collected. Bulk sediment toxicity tests were conducted on the following benthic species: *Hyalella azteca, Chironomous dilutus* (formerly *C. tentans*), and *Lumbriculus variegatus*. Sediment elutriate preparations from these sites were also used in tests on *Pimephales promelas* and *Daphnia magna*. The results of these tests generally showed that growth and survival of test organisms decreased as the HA-28 NOC toxic units[5] increased.

Supplemental bioassay toxicity studies were conducted in 2001 using *H. azteca, C. dilutus*, and *P. promelas* exposed to bulk sediments collected from four contaminated stations and two reference stations (SEH 2002). Parallel tests were conducted utilizing a dilution methodology in which various proportions of sediments from impacted sites were mixed with sediments from reference sites to obtain a range of exposure concentrations.

The results of the 2001 sediment bioassay testing is summarized in Table 3-2. In some instances control and reference station survival was less than test acceptance criteria. These results are discussed further in Section 5.

Test results were evaluated for effects on survival and growth, and graphically compared to PAH toxic units. Statistically significant differences in survival and/or growth between each sample were documented. The SEH report concluded that toxic effects appeared to correlate well to the magnitude of toxic units. SEH concluded that results from both the bulk sediment dilution tests and the sediment elutriate dilution tests supported the exposure concentration/effects characterization.

[5] The Toxic Unit (TU) approach compares the dry weight or Normalized to Organic Carbon (NOC) concentrations of the contaminant, in this case total PAHs, to the Effects Range-Median (ERM) value for total PAHs in a 28 day bioassay with *Hyalella azteca* (HA). Thus a concentration of total PAHs equal to the HA-28 ERM value would be one toxic unit.

Table 3-2. Summary of 2001 SEH Sediment Bioassays for Sandy Stations (as reported).

Test*	No Observed Adverse Effects Concentration (NOEC)		Lowest Observed Adverse Effects Concentration (LOEC) = reduced growth or mortality > 20%	
	Total PAHs µg/g	Total PAHs (NOC) µgPAHs/g OC	Total PAHs µg/g	Total PAHs (NOC) µgPAHs/g OC
CT-10	16.2	735	79.9	3996
PP-7	79.9	3996	249.4	9978
HA-28	249.4	9978	823.1	4842
HA-28 w/UV	16.2	735	79.9	3996

*CT-10 = 10 day *Chironomous dilutus* bioassay

PP-7 = 7 day *Pimephales promelas* bioassay

HA-28 = 28 day *Hyalella azteca* bioassay

HA-28 w/UV = 28 day *Hyalella azteca* bioassay under UV light

SEH also reported that comparison of phototoxic PAH concentrations at the Site to reference levels in the literature indicated the potential for phototoxic effects at the Site. Phototoxicity studies using UV light were performed in 1998 and 2001 in conjunction with standard toxicity test organisms exposed to bulk sediment or sediment elutriate samples collected from the Site. While there was no documentation of how well the UV regime during the bioassay compared to what ecological receptors would be exposed to at the Site, SEH concluded that under the conditions in which the bioassay was conducted there was evidence of enhanced phototoxicity effects for benthic organisms, zooplankton, and fish larvae.

3.2.5 Risk Characterization

SEH concluded from these various lines of evidence that a strong potential exists for ecological risks from exposure to contaminated sediments in the bioactive zone and contaminated surface water over this zone. The lines of evidence they used to support this conclusion included: 1) PAH concentrations in sediments exceeding several sediment effects benchmarks; 2) evidence from field studies of benthic community impairment in the contaminated areas; 3) results of standard and photo-enhanced bioassay tests that indicated that the likelihood of ecological effects increase with exposure to increased contaminant concentrations in sediments and surface waters over the sediments; 4) the exceedances of secondary acute and chronic water quality criteria in one surface water sample collected during heavy wave action, based on field sampling and elutriate studies; 5) sediment concentrations of PAHs similar to those at other sites where bioaccumulation and mutagenic effects have been observed in fish; and 6) evidence of low molecular weight PAHs in some fish tissues collected from the Site.

The risk characterization also concluded that levels of PAHs in subsurface sediments are higher than in the bioactive zone and that future disturbance and exposure of the deeper contaminated sediments to the sediment-water interface and water column by either natural (e.g., storms, ice scouring) or uncontrolled anthropogenic (e.g., boat prop wash, shoreline maintenance) forces could potentially release contaminants from subsurface sediments and transport them from the Site.

The 2001 ERA (SEH 2002) also proposed Preliminary Remediation Goals (PRGs) for the contaminated substrates present (wood chips and sand) that were based on the results of these lines of evidence.

3.2.6 Contaminants of Potential Concern

SEH (1998) screened data on contaminants found in sediment samples collected in 1996 against several sediment quality benchmarks, including those developed by the Ontario Ministry of the Environment (Persaud 1993) and Long and Morgan (1991). Concentrations of most PAHs, as well as total PAHs, and some VOCs exceeded screening values. Metals found in this sampling campaign did not exceed guideline values at any location (SEH 2003); cyanide exceeded a sediment quality guideline in one location.

Further sampling in 2001 detected phenolic compounds in a few samples although these were not specifically screened against sediment quality benchmarks.

SEH (2003) reported additional screening was conducted for contaminants associated with surface sediments collected during 2003. In addition to exceeding sediment quality benchmarks for PAHs and some VOCs (primarily benzene, toluene, ethylbenzene, and xylenes [BTEX]), it was concluded that copper, lead, mercury, zinc and cyanide also exceeded some sediment quality benchmarks. SEH (2003) concluded that COPCs for the RI studies should include VOCs, SVOCs and copper, lead, mercury, zinc, and cyanide.

No screening of contaminants in other media was conducted in these previous risk assessments.

As part of this BERA, all media were re-screened to select COPCs (See Section 3.4).

3.3 SUMMARY OF STUDIES CONDUCTED FOR THE REMEDIAL INVESTIGATION

As part of this RI, a number of investigations were conducted and the results were used, along with historical information, to support this BERA. All of the historical and current data were used as discussed below to screening for COPCs (Appendix A). Investigations conducted during this RI included:

1) Surface soil samples collected in the vicinity of Kreher Park (See RI report URS 2006a);
2) Sediment samples collected as part of the supplemental sediment sampling and sediment quality triad investigations (Appendix B);
3) Sediment toxicity testing (Appendix B);
4) Benthic macroinvertebrate community studies (Appendix B);
5) Collection of fish tissue (Appendix C);

6) Surface water collection (Appendix D); and
7) Characterization of wetlands and terrestrial habitats (Appendix E).

The details of these investigations are in the reports appended to this BERA or in other reports submitted separately to USEPA as cited above.

3.4 NATURE AND EXTENT OF CONTAMINATION

The Site has been the subject of numerous investigations. Previous investigations have identified contamination at Kreher Park and in near shore sediments. Contaminated near shore sediments are located within the inlets created by the jetty and marina extension as discussed in Section 2.1.

3.5 SCREENING OF CONTAMINANTS OF POTENTIAL CONCERN

As the first task in the Baseline Problem Formulation, data for all media, including all historical data, were screened to select COPCs. Screening was conducted using the following benchmarks using the maximum concentration measured:

- **Sediment:** Contaminants in sediment were screened using Wisconsin's sediment quality guidelines (WDNR 2003). If benchmarks for Site contaminants were not available from WDNR the following were used, in order of precedence: USEPA Region V Ecological Screening Levels (ESLs) (USEPA 2003a), TLM=Target Lipid Model (DiToro and McGrath 2000), T50 =Logistic model point estimate of T50 concentrations (concentration at which 50% of samples are predicted to be toxic; Field et al. 2002), NOAA Screening Quick Reference Table (SQuiRT-http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.html), and other available sources.
- **Surface Water:** Region V ESLs (USEPA 2003a) were used as the primary source of screening criteria. If ESLs were not available, then the following criteria were used, in order of precedence: ORNL Tier II values, USEPA Region IV Water Quality Standards and structure-activity relationships using chronic values for fish (ECOSAR).
- **Soil:** USEPA Ecological Soil Screening Levels (ECO-SSLs) (USEPA 2003b; 2005a) were the primary screening criteria for evaluating soils. If ECO-SSLs were not available, then the following criteria were used, in order of precedence: Region V ESLs (USEPA 2003a) and other available sources.

Because USEPA advises that some chemicals that also function as nutrients, (e.g., calcium, magnesium, sodium and potassium) typically pose no ecological risk when present at relatively low concentrations that allow them to function in this manner, these chemicals were not screened.

If any PAH exceeded its individual screening criterion, PAHs as a group were retained as COPCs because it was considered that the mode of action is similar for all PAHs and their toxicity additive (See Section 5).

A summary of media specific screening criteria used to re-screen contaminants detected in Site samples are provided in Table 3-3, Table 3-4 and Table 3-5.

Table 3-3. Screening Criteria Selected for the Re-Screening of COPCs in Surface Water.

Analyte	Criteria (µg/L)	Source[1]
VOCs		
1,2,4-Trimethylbenzene	438	ECOSAR ChV (fish)
1,3,5-Trimethylbenzene	438	ECOSAR ChV (fish)
Benzene	11.4	Region V ESL
Ethybenzene	14	Region V ESL
Sec-Butylbenzene	263	ECOSAR ChV (fish)
Styrene	32	Region V ESL
Toluene	253	Region V ESL
Total Xylenes	27	Region V ESL (sum of isomers)
PAHs		
1-Methylnaphthalene	433	ECOSAR ChV (fish)
1-Methlyphenanthrene	56	ECOSAR ChV (fish)
2,3,5-Trimethylnaphthalene	58	ECOSAR ChV (fish)
2,6-Dimethylnaphthalene	161	ECOSAR ChV (fish)
2-Methylnaphthalene	433	ECOSAR ChV (fish)
Acenaphthene	38	Region V ESL
Acenaphthylene	4840	Region V ESL
Anthracene	0.035	Region V ESL
Benzo(a)anthracene	0.025	Region V ESL
Benzo(a)pyrene	0.014	Region V ESL
Benzo(b)fluoranthene	0.42	Reg IV WQS
Benzo(e)pyrene	0.014	same as B(a)P
Benzo(g,h,i)perylene	7.64	Region V ESL
Benzo(k)fluoranthene	0.14	Reg IV WQS
Biphenyl	14	OSWER Tier II
Chrysene	0.07	Reg IV WQS
Dibenz(a,h,)anthracene	0.04	Reg IV WQS
Fluoranthene	1.9	Region V ESL
Fluorene	19	Region V ESL
Indeno(1,2,3-cd)pyrene	4.31	Region V ESL
Naphthalene	13	Region V ESL
Perylene	0.006	ECOSAR ChV (fish)
Phenanthrene	3.6	Region V ESL
Pyrene	0.3	Region V ESL

Notes:
1. Region V ESL, USEPA Region V Ecological Screening Levels
Region IV WQS, USEPA Region IV Water Management Division Screening List
ECOSAR, Structure-activity relationships using chronic values for fish

Table 3-4. Screening Criteria Selected for the Re-Screening of COPCs in Sediment.

Analyte	Units	Criteria			Source[1]
		TEC	MEC	PEC	
VOCs					
1,2,4-Trimethylbenzene	µg/kg OC	1147			TLM[2]
1,3,5-Trimethylbenzene	µg/kg OC	1147			TLM[2]
Benzene	µg/kg dw @ 1%OC	57	83.5	110	WDNR 2003
Ethybenzene	µg/kg	175			Region V ESL
Sec-Butylbenzene	µg/kg dw @ 1%OC	25	37.5	50	WDNR 2003
Styrene	µg/kg OC	254			Region V ESL
Toluene	µg/kg dw @ 1%OC	890	1345	1800	WDNR 2003
Total Xylenes	µg/kg dw @ 1%OC	25	37.5	50	WDNR 2003
PAHs					
1-Methylnaphthalene	µg/kg		94.00		T50
1-Methlyphenanthrene	µg/kg		112		T50
2,3,5-Trimethylnaphthalene	µg/kg OC	988.0			TLM[3]
2,6-Dimethylnaphthalene	µg/kg		133.0		T50
2-Methylnaphthalene	µg/kg		120.0	240.0	BC
Acenaphthene	µg/kg dw @ 1%OC	6.7	48.0	89.0	WDNR 2003
Acenaphthylene	µg/kg dw @ 1%OC	5.9	67.0	128.0	WDNR 2003
Anthracene	µg/kg dw @ 1%OC	57.2	451.0	845.0	WDNR 2003
Benzo(a)anthracene	µg/kg dw @ 1%OC	108.0	579.0	1050.0	WDNR 2003
Benzo(a)pyrene	µg/kg dw @ 1%OC	150.0	800.0	1450.0	WDNR 2003
Benzo(b)fluoranthene	µg/kg dw @ 1%OC	240.0	6820.0	13400.0	WDNR 2003
Benzo(e)pyrene	µg/kg dw @ 1%OC	150.0	800.0	1450.0	WDNR 2003
Benzo(g,h,i)perylene	µg/kg dw @ 1%OC	170.0	1685.0	3200.0	WDNR 2003
Benzo(k)fluoranthene	µg/kg dw @ 1%OC	240.0	6820.0	13400.0	WDNR 2003
Biphenyl	µg/kg		73.0		T50
Chrysene	µg/kg dw @ 1%OC	166.0	728.0	1290.0	WDNR 2003
Dibenz(a,h,)anthracene	µg/kg dw @ 1%OC	33.0	84.0	135.0	WDNR 2003
Fluoranthene	µg/kg dw @ 1%OC	423.0	1327.0	2230.0	WDNR 2003
Fluorene	µg/kg dw @ 1%OC	77.4	307.0	536.0	WDNR 2003
Indeno(1,2,3-cd)pyrene	µg/kg dw @ 1%OC	200.0	1700.0	3200.0	WDNR 2003
Naphthalene	µg/kg dw @ 1%OC	176.0	369.0	561.0	WDNR 2003
Perylene	µg/kg OC	812.0			TLM[3]
Phenanthrene	µg/kg dw @ 1%OC	204.0	687.0	1170.0	WDNR 2003
Pyrene	µg/kg dw @ 1%OC	195.0	858.0	1520.0	WDNR 2003
Total PAHs	µg/kg dw @ 1%OC	1610.0	12205.0	22800.0	WDNR 2003
Other SVOCs					
Cresols, m- & p-	µg/kg	52.4			Region V ESL
Cresol, o-	µg/kg	55.4			Region V ESL
Dibenzofuran	µg/kg dw @ 1%OC	150.0	365.0	580.0	WDNR 2003
Phenol	µg/kg dw @ 1%OC	4200.0	8100.0	12000.0	WDNR 2003
Metals					
Aluminum	µg/g	25500.0			SQuiRT
Antimony	µg/g	2.0	13.5	25.0	WDNR 2003
Arsenic	µg/g	9.8	21.4	33.0	WDNR 2003
Barium	µg/g	48.0			OR
Beryllium	µg/g	122.0			OR
Cadmium	µg/g	1.0	3.0	5.0	WDNR 2003
Chromium	µg/g	43.0	76.5	110.0	WDNR 2003
Cobalt	µg/g	43.4			Region V ESL
Copper	µg/g	32.0	91.0	150.0	WDNR 2003
Iron	µg/g	20000.0	30000.0	40000.0	WDNR 2003
Lead	µg/g	36.0	83.0	130.0	WDNR 2003
Manganese	µg/g	460.0	780.0	1100.0	WDNR 2003
Mercury	µg/g	0.2	0.6	1.1	WDNR 2003
Nickel	µg/g	23.0	36.0	49.0	WDNR 2003
Selenium	µg/g	1.0			SQuiRT
Silver	µg/g	1.6		2.2	WDNR 2003
Thallium	µg/g	0.7			OR
Vanadium	µg/g	57.0			SQuiRT
Zinc	µg/g	120.0	290.0	460.0	WDNR 2003
Cyanides	µg/g	0.1			Region V ESL

Notes:

1, WDNR 2003, Consensus-Based Sediment Quality Guidelines Recommendations for Use & Application Interim Guidance (WDNR 2003)
Region V ESL, USEPA Region V Ecological Screening Levels
TLM, Target Lipid Model (DiToro and McGrath 2000-See text)
T50, Logistic model point estimate of T50 concentrations (concentration at which 50% of samples are predicted to be toxic, Field et al 2002)
SQuiRT, NOAA Screening Quick Reference Tables
BC, Critria for Managing Contaminated Sediment in British Columbia. MWLAP 2004
OR, Oregon DEQ Level 2 Screening Level Values

2, Critical body residue (CBR) VOCs is 6.94 umol/g lipid

3, Critical body residue (CBR) for PAHs is 3 79 umol/g lipid

Table 3-5. Screening Criteria Selected for the Re-Screening of COPCs in Soil.

Analyte	Criteria[1]	Source[2]
VOCs (µg/kg)		
1,2,4-Trimethylbenzene	NE	
1,3,5-Trimethylbenzene	NE	
Benzene	255	Region V ESL
Ethybenzene	5160	Region V ESL
Sec-Butylbenzene	NE	
Styrene	4690	ORNL 1997
Toluene	5450	Region V ESL
Total Xylenes	10000	Region V ESL
PAHs (µg/kg)		
1-Methylnaphthalene	NE	
1-Methlyphenanthrene	NE	
2,3,5-Trimethylnaphthalene	NE	
2,6-Dimethylnaphthalene	NE	
2-Methylnaphthalene	NE	
Acenaphthene	682000	Region V ESL
Acenaphthylene	682000	Region V ESL
Anthracene	1480000	Region V ESL
Benzo(a)anthracene	5210	Region V ESL
Benzo(a)pyrene	1520	Region V ESL
Benzo(b)fluoranthene	59800	Region V ESL
Benzo(e)pyrene	1520	BaP surrogate
Benzo(g,h,i)perylene	119000	Region V ESL
Benzo(k)fluoranthene	148000	Region V ESL
Biphenyl	60000	ORNL 1997
Chrysene	4730	Region V ESL
Dibenz(a,h,)anthracene	18400	Region V ESL
Fluoranthene	122000	Region V ESL
Fluorene	122000	Region V ESL
Indeno(1,2,3-cd)pyrene	109000	Region V ESL
Naphthalene	99.4	Region V ESL
Perylene	NE	
Phenanthrene	45700	Region V ESL
Pyrene	78500	Region V ESL
Total PAHs	NE	
Other SVOCs (µg/kg)		
Cresols, M & P	7950.00	Region V ESL
Cresol,O	40400.0	Region V ESL
Dibenzofuran	NE	
Phenol	120000.0	Region V ESL
Metals (µg/g)		
Aluminum	NE	USEPA 2005
Antimony	0.27	USEPA 2005
Arsenic	18.0	USEPA 2005
Barium	330.0	USEPA 2005
Beryllium	21.0	USEPA 2005
Cadmium	0.36	USEPA 2005
Chromium	26.0	USEPA 2005
Cobalt	13.0	USEPA 2005
Copper	54.0	USEPA 2003b
Iron	NE	USEPA 2005
Lead	11.0	USEPA 2005
Manganese	152.0	USEPA 2003b
Mercury	0.1	Region V ESL
Nickel	48.0	USEPA 2003b
Selenium	0.028	USEPA 2003b
Silver	4.0	Region V ESL
Thallium	0.057	Region V ESL
Vanadium	78.0	USEPA 2005
Zinc	120.0	USEPA 2003b
Cyanides	1.3	Region V ESL

Notes:
1, NE= Not Established
2, Region V ESL, USEPA Region 5 Ecological Screening Levels (USEPA 2003a)
USEPA 2005, Ecological soil screening levels (ECO-SSLs).
USEPA 2003b, Draft Ecological Soil Screening Levels (ECO-SSLs)
ORNL 1997, Oak Ridge National Laboratory (Efroymson et al 1997).

The results of this re-screening is presented in Appendix A and summarized in Table 3-6. These chemicals were retained for further analysis in the BERA.

Table 3-6. List of COPCs by Medium Based upon the Maximum Detected Concentration.

Surface Water	Sediment	Soil
None	Total PAHs	Total PAHs
	Dibenzofuran	Benzene
	m-Cresol	Antimony
	o-Cresol	Barium
	p-Cresol	Cadmium
	1,2,4-Trimethylbenzene	Chromium
	1,3,5-Trimethylbenzene	Copper
	Benzene	Lead
	Ethylbenzene	Manganese
	Toluene	Mercury
	Total Xylenes	Selenium
	Antimony	Silver
	Arsenic	Thallium*
	Barium	Zinc
	Cadmium	Cyanide
	Copper	
	Iron	
	Lead	
	Manganese	
	Mercury	
	Nickel	
	Selenium	
	Silver	
	Thallium	
	Vanadium	
	Zinc	
	Cyanide*	

* Eliminated as a COPC based upon frequency of detection (<5%).

3.6 REFINEMENT OF CONTAMINANTS OF CONCERN

This initial list of COPCs was reviewed to determine whether any COPCs could be eliminated based upon relatively infrequent, less than 5%, detection. Cyanide was eliminated as a sediment COPC and thallium was eliminated as a soil COPC based upon this criterion.

3.7 OTHER STRESSORS OF POTENTIAL CONCERN

In addition to contaminants that may be related to the MGP that operated on the Site there were several other historical operations that used the Site. The following is a preliminary list of activities that have resulted in physical and chemical alterations to the habitat that are not directly related to MGP contaminant releases:

1) City-owned parcels of the lakefront were created during the late 1880s through the latter part of the 1980s by the uncontrolled placement of wood wastes, soil, sand, and industrial and municipal demolition waste material into Chequamegon Bay;
2) Sawdust and wood waste from a series of sawmills that operated on the Ashland site from the early 1880s until about the mid-1930s were dispersed by natural forces, rain, flooding, storms and ice throughout Chequamegon Bay;
3) Log rafting and timber loading led to bark and wood waste accumulating to depths of many feet in various places in Chequamegon Bay;
4) Releases of chemicals from wood wastes and releases from secondary wood processing facilities including shingle victories and **possible** wood treatment operations; and
5) Discharges of chemicals from the construction, expansion and operation of the Ashland WWTP.

These other sources and physical alterations of Site habitat may have some of the same effects as Site contaminants. While it may not be possible to differentiate the effects of these other stressors relative to the effects from Site contaminants it should be understood that they are potentially contributing stressors. This is particularly true of the physical alterations to the nearshore aquatic habitat resulting from the presence of wood "mulch" and wood waste overlaying the sediments.

As reported by SEH (1998b), wood waste is found throughout the Ashland site in thickness averaging about 0.26 meters (~ eight inches) and ranging from 0-2 meters, "the wood chip layer extends from the Ashland Harbor shoreline out to the harbor mouth (approximately 270 m) and is deepest at the east end of the harbor (up to 2.1 m), rapidly declining to a thickness of between 15 and 24 cm [six-eight inches] over the majority of the remainder of the harbor." Further observations made during the RI sampling by underwater video and side scan sonar (URS 2006a) have provided more information about this wood "mulch" and based upon this information approximately 95% of the substrate in the Site area is covered by wood "mulch" and wood waste.

In addition to the potential direct effects to habitat quality from all of this wood covering the bottom, there are also indirect effects that may include release of excess nitrogen (which may exist in the form of ammonia, nitrate and/or nitrite), phosphorous (in the form of phosphate) and sulfides. The presence of wood mulch on top of the sediment bed can also increase biological oxygen demand and materially affect the dissolved oxygen levels at the sediment-water interface and at shallow depths within the sediment. Both the presence of excess nutrients, soluble organics and changes to dissolved oxygen can cause changes to the environment for both benthos and fish and may limit their presence in certain areas. Other physical changes related to changes in lake level, storms and sediment deposition dynamics also potentially can modify the characteristics of the aquatic environment and thus exert an effect on aquatic receptors.

The former Ashland WWTP operated at the site of the former sawmill (at the end of Prentice Avenue), adjacent to the highest levels of sediment contaminants, until approximately 1990. It is likely that the construction and operation of the WWTP resulted in various chemicals, including metals and SVOCs, being discharged into waters now included within the Site boundary.

3.8 ENVIRONMENTAL SETTING

3.8.1 Aquatic Habitat Description

The littoral areas of Chequamegon Bay within the Site boundaries have a relatively smooth and gradually sloping bottom to depths of around 10 feet deep. As reported by SEH (2002), "although the harbor area is open to Lake Superior, the limnology is more comparable to a warm water lake than the pelagic, oligotrophic zone typical of [deeper areas of] Lake Superior." The lake bottom in the Site area is primarily sandy substrate although, as described above, it is mostly covered by variable depth layers of wood debris, tree branches, wood slabs, lumber and logs. The presence of this wood has significant implications for the structure of the benthic community, including emergent plants, periphyton infauna and epifauna. The planktonic and fish community is probably somewhat less affected by the presence of the wood.

3.8.1.1 Aquatic Plants

No study of the aquatic plant community in the Site waters has been conducted. Observations made during the RI sampling suggest it is neither extensive nor diverse. Some limited submerged vegetation was observed and recorded by underwater video. The presence of the wood "mulch" and the fact that the smaller particles of wood are likely mobile, moving in response to wave action, precludes the proliferation of emergent vegetation or periphyton species that would typically live in this type of habitat.

3.8.1.2 Aquatic Animals

The benthos was the only group of animals that utilize this aquatic habitat that was studied during this RI and earlier studies conducted to support the ecological risk assessment (SEH 1998). The results of the benthic community study conducted as part of the RI indicate that the benthic community in the Site area is largely dominated by oligochaetes, molluscs, chironomids and crustaceans (Appendix B). The dominant taxa were chironomids which made up an average 32.6% (maximum 84 to 91% in the five replicate samples from Sand Reference Station SQT12) of the abundance in each sample. In all, 58 taxa of chironomids were identified. The next most abundant taxa were a sabellid polychaete (*Manayunkia speciosa*), oligochaetes (primarily tubificids), nematodes, an isopod (*Caecidotea racovitzai*), amphipods (including *Gammarus* *fasciatus*), the unionid snail (*Amnicola limnosa*), sphaerid clams (including *Pisidium* spp.), mayflies, and caddisflies. Together these ten taxa made up approximately 94% of the total number of individuals (Appendix B). Chironomids and tubificids alone made up approximately 50% total number of individuals. Aquatic insects made up 75% of the taxa; the majority of these were chironomid taxa.

For characterization of the fish community we have to rely on studies conducted by USGS over the years of 1973 to 1996 (Hoff and Bronte 1998). These studies as well as observations by WDNR have produced a list of about 49 species likely to utilize waters in or near the Site for spawning, rearing or feeding (See Table 6 in SEH 2002). Of these, the USGS concluded that about seven species are more likely to utilize the shallow Site waters: smallmouth bass, logperch, mimic shiner, silver redhorse, black bullhead, johnny darter and spottail shiner. Based upon observations made during the RI fish tissue sampling, the list of those species frequenting the Site waters should be amended to include rock bass, walleye, common carp, shorthead redhorse, longnose sucker, white sucker, brown bullhead, rainbow smelt, and trout-perch. To a lesser extent, northern pike, green sunfish, pumpkinseed, yellow perch and juvenile coho salmon have also been observed in the Site waters.

Although SEH (1998, 2002) mentions that either zooplankton or phytoplankton surveys were conducted in the 1970's to support a dredging project, no data on plankton are presented in their two reports and a search for other descriptions of the plankton community found in Ashland Harbor was not productive.

3.8.2 Upland Habitat Description

On June 15, 2005, a characterization of terrestrial and wetland habitats on the Site was conducted. The results of that characterization are reported in Appendix E and summarized in the following sections.

3.8.2.1 Terrestrial Habitat Description

There are five main habitat types on the upland portion of the Site. These include wooded/shrub, open field, developed/lawn, wetland and lake edge. The Canadian National Railroad runs parallel to the bluff, approximately 30 feet lakeward of the bluff. Vegetation between the tracks and the bluff is a 30- to 50-year-old strip of woodland consisting of green ash, oak, boxelder and cottonwood. Downslope vegetation parallels the railroad tracks for the most part, and consists of 10- to 20-year-old boxelder and shrubs such as raspberry, dogwood, willow, honeysuckle, red elderberry, green ash, and grape. The entire wood/shrub area is approximately 1.55 acres in size.

The open field between the wooded area and Chequamegon Bay is approximately 1 acre and consists primarily of open field made up of brome, thistle, dandelion and timothy. This area is traversed by a lawn area that contains some park amenities, such as picnic tables and benches. The marina parking lot on the western edge of the site is gravel. There is one small wetland area located east of the parking lot, near the border of the wooded/shrub and open field areas.

North of Marina Drive consists of primarily lawn, which gives way to the sandy/rocky shore edge. There is another shrub area approximately 2.07 acres in size located to the east/northeast of the former wastewater treatment plant. Lake edge habitat consists of a fairly narrow strip of sand

and rocks along Chequamegon Bay in some areas, with lawn vegetation going all the way to the water's edge in others.

The developed/lawn areas would typically be home to songbirds, squirrels, rabbits, and other small rodents that are adapted to an urban setting. The lakeshore typically provides habitat for a wide range of birds and mammals, however, in the immediate Site area, lakeshore habitat is limited due to the location of the marina (high boat traffic area) and shoreline development (riprap).

3.8.2.2 Wetland Habitat Description

No wetlands on the Site were identified on National Wetland Inventory or Wisconsin Wetlands Inventory maps. There is no soil survey data for the project site, as most of the Site consists of dredge and fill material deposited in the 1900s. Field observations resulted in the identification and delineation of one wetland area, using the U.S. Army Corps of Engineers (USACE) Wetlands Delineation Manual (Appendix E).

The wetland is located east of the Ellis Avenue Marina parking lot, along the edge of the wooded/shrub area. A small part of the wetland is south of the railroad tracks and this is connected to the remainder of the wetland to the north of the railroad tracks by a culvert. This wetland is approximately 0.24 acre in size with a majority (90%) of the wetland consisting of the area north of the railroad tracks. Dominant plant species included reed canary grass *(Phalaris arundinacea)*, stinging nettle *(Urtica dioica)*, sandbar willow *(Salix interior)* and Canada thistle *(Cirsium arvense)*. All but the thistle are considered wetland species. Depth to saturated soil was approximately six inches and hydric, clayey soils were present. The wetland appears to be receiving water through a seep south of the tracks. It runs through a small ditch on the south side of the tracks passing through a culvert and flowing into the north basin. The basin is primarily a wet meadow wetland with a fringe of sandbar willow. It had a drain tile beneath the wetland, though now that drain tile has been exposed and broken allowing water to freely flow to the north toward Lake Superior. The wetland boundary was determined by presence of vegetation and hydric soils.

A functional values assessment was completed for this wetland based upon USACE protocols. The wetland scored low in significance for Floral Diversity, Wildlife Habitat, Fishery Habitat, Groundwater and Aesthetics/Recreation/Education. The wetland does provide a high function for Water Quality Protection from upslope runoff and provides moderate flood/stormwater attenuation function. Documentation of this assessment is also included in Appendix E.

3.8.2.3 Wetland and Terrestrial Plants and Animals

Common plants and animals either observed or expected to utilize the wetland and terrestrial habitats on the Site are summarized in Table 3-7. See Appendix E for details on what was actually observed and what was assumed to be there based upon regional species lists and habitat types.

Table 3-7. Wildlife Species Observed or Expected to Utilize Site Upland or Terrestrial Habitats.

Common Name	Scientific Name	Site Habitat
Gray catbird	*Dumetella carolinensis*	Shrub/wooded
Common crow	*Corvus brachyrhynchos*	Developed
House sparrow	*Passer domesticus*	Developed
American robin	*Turdus migratorius*	Wooded
Brown-headed cowbird	*Molothrus ater*	Wooded
Herring gull	*Larus argentatus*	Lake edge
Cedar waxwing	*Bombycilla cedrorum*	Wooded
Common starling	*Sturnus vulgaris*	Developed
Ovenbird	*Seiurus aurocapillus*	Wooded
Red-winged blackbird	*Agelaius phoeniceus*	Open field and Wetland
Pigeon	*Columba fasciata*	Developed
Mourning dove	*Zenaida macroura*	Developed
Chipmunk	*Tamias minimus*	Developed
Woodchuck	*Marmota monax*	Developed

3.8.2.4 Special Status Species

Rare, endangered, or threatened species of plants and animals are treated more conservatively than more common plants and animals in risk assessments. Therefore, it was important to ascertain if any of these species exist at or near the Site. Letters requesting information on rare, threatened and endangered species were sent to the U.S. Fish and Wildlife Service (USFWS) and Wisconsin Department of Natural Resources (WDNR) on July 29, 2005. The USFWS maintains a list of federally-protected species, while the WDNR maintains a list of state-protected species. These agencies are responsible for identifying and enforcing necessary mitigation measures should any species potentially be affected by a proposed project.

The WDNR concluded that there are 7 known occurrences of rare species or natural communities within an approximate 2-mile radius around the project site and within five miles for aquatic species. The species listed includes two birds, one diving beetle and four plants.

The birds were the merlin (*Falco columbarius*) and the common tern (*Sterna hirundo*), which were the only species found near the project area. Neither bird species has habitat within the project area and further surveys or protocols for these species are not necessary. The diving beetle is recorded in Bay City Creek, which will not be impacted by this project. The plants are all wetland species and were not in the project site or adjoining properties.

The USFWS provided a list of species that are known to occur within Ashland County, but indicated that no federally-listed species or critical habitat is known to occur in the project site or within a 2-mile radius.

3.9 RISK MANAGEMENT GOAL

As defined by USEPA (2001a), "a *risk management goal* is a general statement of the desired condition or direction of preference for the entity to be protected.

The following risk management goal is proposed:

> **Maintenance (or provision) of soil, sediment and water quality as well as food source, and habitat conditions capable of supporting a "functioning ecosystem" for the aquatic and terrestrial plant and animal populations (including individuals of protected species) inhabiting or utilizing the Ashland/NSP Waterfront Superfund Site area.**

The proposed assessment endpoints presented in Section 3.10 were developed based upon this risk management goal.

3.10 CONCEPTUAL SITE MODEL

3.10.1 Contaminant Fate and Transport

Available information provided in prior reports was reviewed to evaluate the potential fate and transport mechanisms that may result in complete exposure pathways. The evaluation focused on identifying whether the following primary components of a complete exposure pathway were present in the AOIs:

- Source of contamination;
- Release and transport mechanism;
- Contact point and exposure media;
- Routes of entry; and,
- Key receptors.

Each of these components is discussed below.

3.10.2 Source of Contamination

As discussed in Section 2.1 various industries have operated on the Site. In addition to the lumbering operations, the Site area has also been used as:

- A "dump" for solid waste, fly ash, and dredge spoils by property owners, residents, and the United States Army Corps of Engineers;
- The City of Ashland WWTP;
- A manufactured gas plant; and
- Secondary wood processing plants including possible wood treatment and shingle manufacturing.

These operations have resulted in both chemical and physical alterations of the Site area, particularly in aquatic portions of the Site.

3.10.3 Release and Transport Mechanisms

One or more of the following release and transport mechanisms potentially may affect the concentration and spatial distribution of COPCs at and around the Site:

- Dissolution and leaching into groundwater underlying the Site;
- Migration of dissolved COPCs in groundwater to sediment and surface water in Chequamegon Bay, and its attenuation by dilution/dispersion, sorption and biodegradation;
- Suspension and windblown transport of COPCs adsorbed to particles in ambient air;
- Transport of COPCs adsorbed to soil particles via surface water runoff;
- Backfilling of soils, wood waste and construction debris; and
- Trophic transfer of COPCs that are incorporated in the aquatic and terrestrial food chains.

The potential for COPCs to be released and transported from the sources to points of contact with ecological receptors depends on their physicochemical properties, ambient concentrations, and their spatial distribution. Surface water runoff and groundwater infiltration are of particular importance to soluble species of contaminants and less important to hydrophobic organic compounds. Hydrophobic compounds, if any, are likely more of an issue in soil, sediment, and food/prey exposure media.

3.10.4 Contact Point and Exposure Media

The potential contact points for ecological receptors are identified below:

- Surface water, surface soil and food/prey in terrestrial habitats; and
- Surface water, sediment and food/prey in aquatic and wetland habitat.

Each of these contact points and their respective exposure media will be addressed in the BERA.

3.10.5 Routes of Entry

The potential routes of entry for ecological receptors are:

- Direct contact: dermal and/or gill absorption;
- Ingestion; and,
- Inhalation.

Adequate ecotoxicity information is available in the scientific literature to address ecological risks associated with the direct contact and ingestion routes of entry. Complete exposure pathways that include these routes are evaluated in this BERA. Available scientific information is not adequate to evaluate complete exposure pathways for inhalation, and this route will represent an uncertainty in the BERA, although exposure of Site ecological receptors to volatile chemicals is considered to be a minor potential issue at this Site.

3.10.6 Toxicology of COPCs

PAHs are the primary COPC that will be addressed in this BERA. PAHs are a diverse class of organic compounds that include about one hundred individual substances containing two or more fused benzene, or aromatic, rings. Low molecular weight (LMW) PAHs have fewer than four rings, while high molecular weight (HMW) PAHs have four or more rings. The LMW PAHs include acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, 2-methylnaphthalene, and phenanthrene. The HMW PAHs include benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenz(a,h)anthracene, fluoranthene, and pyrene.

PAHs are usually present in the environment in complex mixtures of hundreds or even thousands of related compounds (Neff et al. 2005). They may originate from three sources: fossil fuels (petrogenic PAHs), burning of organic matter (pyrogenic PAHs) and transformation of natural organic precursors by diagenic processes (biogenic PAHs).

The behavior of PAHs in the aquatic environment depends on a number of chemical-specific and site-specific factors. The physicochemical properties of PAHs tend to determine their fate in aquatic systems. The PAHs with high aqueous solubilities are less tightly bound to sediments and may be found in surface water. PAHs with lower aqueous solubilities are usually incorporated into the bed sediment, but may be found in surface waters if they are bound to suspended particulates of benthic origin.

While in the water column either in association with colloidal material or suspended particulates, the fate of PAHs tends to be governed by physical hydrodynamic factors, (e.g. advective transport). While in the water column PAHs may be transported to other areas, biodegrade, evaporate, photochemically degrade or may be consumed by water column biota.

Release of some materials such as tar or creosote, which contain a number of PAH compounds, into an aquatic environment can lead to relatively quick incorporation into the sediment milieu. Once in the sediment bed release of LMW PAHs into the overlying water column is possible although the primary fate is biodegradation and biotransformation by benthic organisms (USEPA 1980 as cited by Eisler 2000). The rate of these biodegradation processes vary substantially depending upon the molecular weight of the PAHs and the presence of microbial communities in the sediments. In the absence of penetrating radiation and oxygen (beneath the immediate surface layers) degradation rates are typically slow. As a result, at most historical PAH waste sites, PAHs are found distributed relatively deeply in the sediment column since the rate of sediment deposition exceeds PAH degradation rates.

The presence of PAHs in aquatic ecosystems pose a number of potential risks to aquatic organisms. At sufficiently elevated levels waterborne PAHs can be lethal to water column receptors and long-term exposure to sublethal levels of PAHs in the sediment have been shown to affect survival, growth and reproduction of benthic organisms. USEPA (2002) has recently provided guidance for evaluating the effects of mixtures of PAHs in sediment on benthic organisms. It is based upon equilibrium partitioning (i.e., estimating the bioavailability of PAHs in sediment pore water using equilibrium theory) and a common narcotic mode of action for mixtures of PAHs and other nonionic organic chemicals.

However, USEPA (2002a) acknowledges that this approach could potentially overestimate the bioavailable fraction of PAHs in sediment pore water if there are PAHs in the sediment associated with soot, coke, slag, tar and coal. As recent research into the bioavailability of PAHs in sediment has demonstrated, PAHs associated with these forms of pyrogenic carbonaceous material have very low bioavailability (Accardi-dey and Gschwend 2003; Burgess 2004; Ghosh et al. 2003, Rust et al. 2004). Other authors have shown that the longer PAHs are in contact with organic carbon even from ordinary detritus, the less bioavailable they become.

Other aspects of the fate and transport as well as potential toxicology of PAHs and the other COPCs is discussed in Section 5 (Effects Analysis).

3.10.7 Ecosystems Potentially at Risk

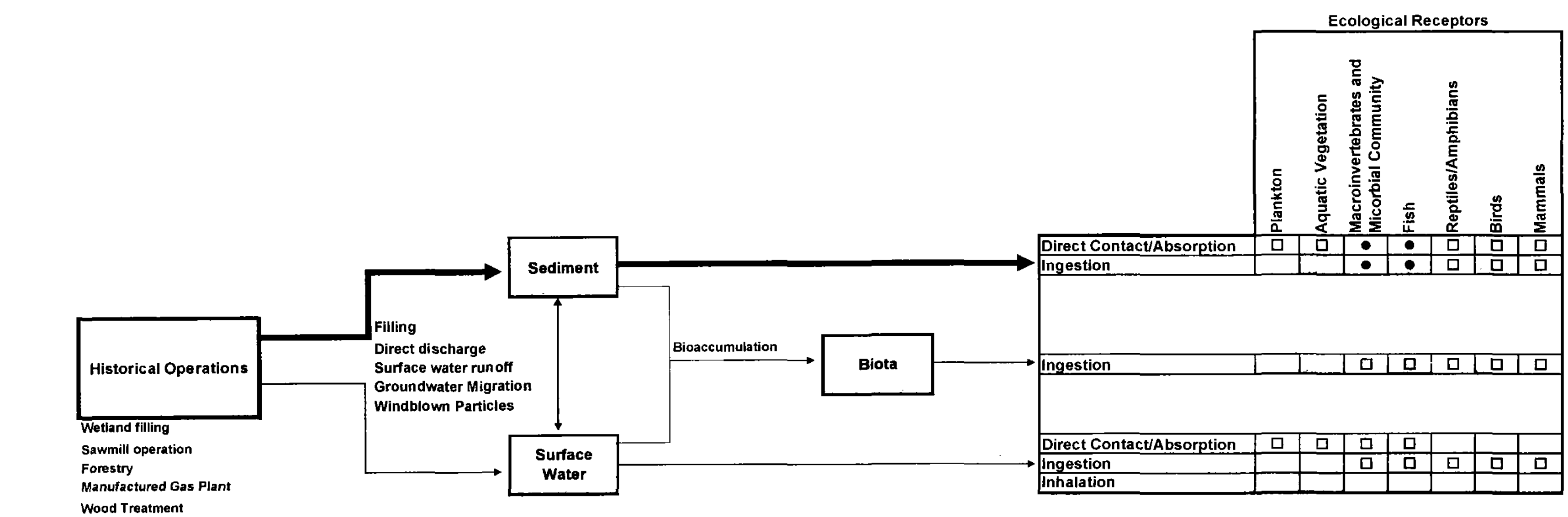
This BERA focuses on the aquatic ecosystem in the Site. The majority of the upland portion of the Site is developed for industrial or residential use or open fields. Not much area within the Site boundaries is undisturbed and the area is managed and used without regard to wildlife habitat. However, as directed by USEPA, the BERA will address potential risk to exclusively terrestrial receptors.

3.10.8 Exposure Pathways

The potential routes of exposure are the means by which chemicals are transferred from a contaminated medium to ecological receptors. The routes by which ecological receptors may be exposed to COPCs in the Site area include:

- Periphyton – direct contact with sediment and surface water;
- Benthic macroinvertebrates – ingestion and direct contact with sediment or surface water;
- Fish – ingestion and direct contact with sediment and surface water;
- Terrestrial plants – direct contact with soil or sediment;
- Soil community – ingestion and direct contact with soil or sediment;
- Amphibians – ingestion and direct contact with surface water and soil or sediment;
- Reptiles – ingestion and direct contact with surface water and soil and sediment; and
- Birds and mammals – ingestion of soil or sediment, surface water, and food.

These potential exposure pathways are illustrated in the Conceptual Site Model (CSM) Figures 3-1 and 3-2. Some exposure pathways have been combined with others or cannot be quantitatively evaluated because of a lack of available information for the exposure evaluation. These will be considered uncertainties in this BERA. Examples of these potential exposure pathways include dermal and inhalation exposures for birds and mammals. Although these pathways are not quantitatively evaluated they are considered relatively minor exposure pathways relative to other exposure pathways.

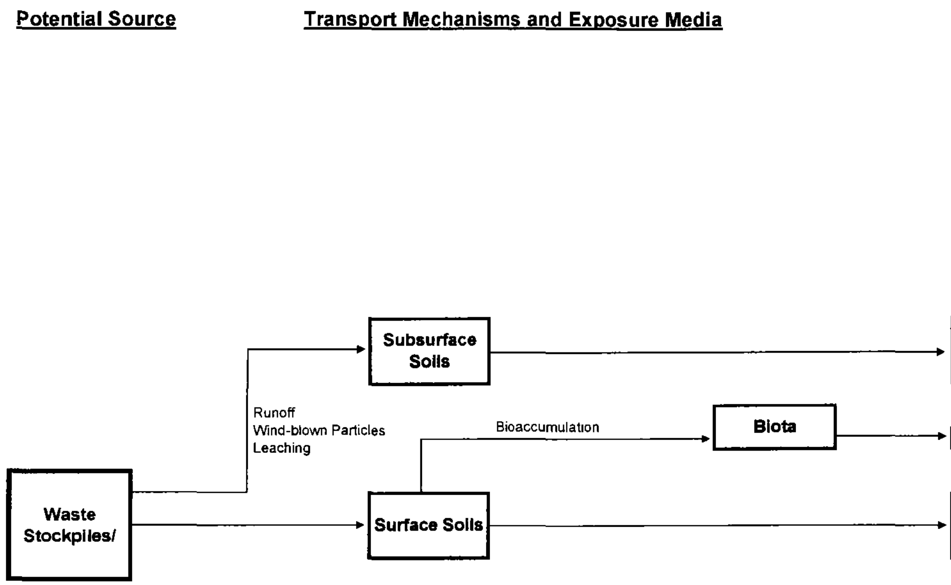


Medium	Exposure Route	Plankton	Aquatic Vegetation	Macroinvertebrates and Micorbial Community	Fish	Reptiles/Amphibians	Birds	Mammals
Sediment	Direct Contact/Absorption	□	□	●	●	□	□	□
Sediment	Ingestion			●	●	□	□	□
Biota	Ingestion			□	□	□	□	□
Surface Water	Direct Contact/Absorption	□	□	□	□			
Surface Water	Ingestion			□	□	□	□	□
Surface Water	Inhalation							

NOTE:
● = Potentially Important Exposure Pathway
□ = Minor Exposure Pathway
Blank = Incomplete Exposure Pathway

FIGURE 3-1

CONCEPTUAL SITE MODEL
AQUATIC EXPOSURE PATHWAYS
Ashland Lakefront Site
Ashland, Wisconsin



Exposure Route

Exposure Medium	Exposure Route	Vascular Plants	Soil Microbes and Soil Invertebrates	Invertivorous Birds (Ground Insects)	Insectivorous Birds (Flying Insects)	Carnivorous Birds	Omnivorous Mammals	Invertivorous Mammals (Ground Insects)	Insectivorous Mammals (Flying Insects)	Carnivorous Mammals
Subsurface Soils	Direct Contact/Absorption	□	□	□				□		
	Ingestion	□	□	□				□		
	Inhalation									
Biota	Ingestion			□	□	□	□	□	□	□
Surface Soils	Direct Contact/Absorption	●	●	●				●		
	Ingestion			□	□	□	□	□	□	□
	Inhalation									

(Column group heading: Ecological Receptors)

NOTE:
NOTE:
● = Potentially Important Exposure Pathway
□ = Minor Exposure Pathway
Blank = Incomplete Exposure Pathway

FIGURE 3-2
SITE CONCEPTUAL MODEL
TERRESTRIAL PATHWAYS
Ashland Lakefront Superfund Site
Ashland, Wisconsin

The following exposure pathways will not be quantitatively evaluated for the following reasons (Table 3-8):

Table 3-8. Exposure Pathways Not Quantitatively Evaluated.

Potential Exposure Pathway	Reason for not Evaluating Quantitatively
Direct contact of periphyton, fish and amphibians with sediment.	Surface water is the primary exposure pathway (no COPC were identified in surface water) and there is inadequate information to quantitatively evaluate direct contact with sediment.
Aquatic invertebrates and fish: Exposure to chemicals through food chain transfer.	Although this is a complete exposure pathway, there is inadequate information to quantitatively evaluate. The evaluation of fish will integrate any food chain transfer taking place at lower trophic levels.
Terrestrial invertebrates: Exposure to chemicals through food chain transfer.	Inadequate information exists to quantitatively evaluate. The evaluation of small mammals and birds will integrate any food chain transfer taking place at lower trophic levels.
Birds and mammals: Exposure to chemicals through dermal adsorption.	Inadequate information exists to quantitatively evaluate. The fur-covered skin of mammals and the feathers of birds limit the direct dermal uptake of chemicals from the environment and this pathway will not be evaluated. Preening and grooming behaviors, however, contribute to the incidental ingestion of soil or sediment, and are included as part of the incidental ingestion exposure pathway.
Birds and mammals: Exposure to chemicals through inhalation.	Inadequate information exists to quantitatively evaluate. It is doubtful that there is sufficient volatilization of sediment-or soil-associated chemicals to result in a threat to bird and mammal receptors. This will be discussed as an uncertainty.

3.11 ASSESSMENT ENDPOINTS, RISK QUESTIONS, MEASUREMENT ENDPOINTS

This section will present specific assessment endpoints as well as associated risk questions and measurement endpoints. Although measurement endpoints are typically introduced in Step 4 of the ERAGS process during the Study Design and Data Quality Objective Process, they are discussed in this section to emphasize the relationship between the assessment endpoints, risk questions, and measurement endpoints.

Assessment endpoints are explicit expressions of the actual environmental value that is to be protected, operationally defined by an ecological entity and its attributes (USEPA 1998). The criteria for selection of assessment endpoints include ecological relevance, susceptibility (exposure plus sensitivity), and relevance to management goals.

Risk questions are questions about the relationships among assessment endpoints and their predicted responses when exposed to contaminants. The risk questions should be based on the assessment endpoints and provide a basis for developing the study design (Step 4) and for evaluating the results of the site investigation in the analysis phase (Step 6) and during risk characterization (Step 7) (USEPA 1997).

A measurement endpoint is a measurable ecological characteristic that is related to the assessment endpoint and is a measure of biological effects (e.g., mortality, reproduction, growth) (USEPA 1997). Measurement endpoints are frequently numerical expressions of observations (e.g., toxicity test results, community diversity measures) that can be compared statistically to a control or reference site to detect adverse responses to a site contaminant.

A line of evidence is, "information derived from different sources or by different techniques that can be used to describe and interpret risk estimates" (USEPA 1998). USEPA (1997) concluded that, in general, there are four possible lines of evidence that can be used to test these risk questions and hypotheses:

1) Comparing estimated or measured exposure levels of contaminants with levels of the contaminants that are known to cause adverse effects to receptors associated with the assessment endpoints;
2) Comparing laboratory bioassays of media from the subject site with artificial media or media from a reference site;
3) Comparing in situ toxicity tests at the subject site with in situ toxicity tests at a reference site; and
4) Comparing observed effects in receptors associated with the subject site with similar receptors at a reference site. This could include population and community studies, for instance.

Each of these lines of evidence can incorporate one or more measurement endpoints that describe the change in the assessment endpoint in response to exposure to a stressor, in this case, a COPC. Lines of evidence proposed for use in this baseline ecological risk assessment include:

Exposure Levels: Concentration Values in Environmental Media

This approach is essentially a predictive line of evidence. By comparing levels of contaminants measured in site media, (e.g., soil, sediment and surface water), or in organisms, (e.g., contaminant levels in fish and invertebrate tissue or in prey ingested by wildlife) to toxicological information from the literature, one can predict the likely response of site-specific ROCs. Uncertainty associated with this approach relates to the differences between the site-specific exposure and the conditions of the study from which the toxicological information was obtained.

Site-Specific Toxicity Data: Laboratory Bioassays

This line of evidence generally uses tests of receptor response to site media, e.g. sediment, soil or water column toxicity bioassays. This approach is often more relevant than the literature in understanding the responses of site receptors to contaminants. However, since site-specific exposure conditions cannot be exactly replicated, nor do test organisms necessarily react to a stressor similar to site receptors, there is some uncertainty associated with this approach.

Direct Observations of Receptor Populations

Direct observations on presence, composition, condition and behavior of receptor populations and communities at the site of interest can also be a fairly direct line of evidence for evaluating the extent of site-related impacts on ecological receptors. The inherent variability in natural populations, however, inevitably introduces uncertainty into interpretation of this line of evidence. Therefore, it is critical that analysis of this line of evidence be sufficiently sensitive to distinguish differences between site and reference populations or communities that may be related to the stressors being evaluated from differences in these populations or communities that are only due to natural variability.

3.11.1 Assessment Endpoints

Nine assessment endpoints have been identified for this BERA. Individual effects level endpoints were selected for protected species; community effects level endpoints were selected for other species. Assessment endpoints are discussed in the following sections.

3.11.2 Aquatic Ecosystem

3.11.2.1 Assessment Endpoint #1: Viability and Function of Benthic Macroinvertebrate Community

The benthic macroinvertebrate community was selected as an assessment endpoint due to its role in energy flow and materials cycling, its potential for exposure to contaminants, and its potential role as a food source for higher trophic level organisms. This assessment endpoint will consider whether the sediment quality at the Site is adequate to support a benthic invertebrate community composition and diversity that is within the range of natural variability of benthic communities in nearby lake habitats in the region and to provide suitable forage for indigenous fish and wildlife species.

Risk Question:

Are concentrations of contaminants in the sediments at the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site sediment.
- Determine the levels of soot, coal, coke and slag which may moderate the bioavailability of PAHs in the sediment.

- Compare concentrations of metals measured in Site sediment to WDNR (2003) sediment quality guidelines for TEC and PEC.
- Determine the levels SEM:AVS in the sediment. This is a measure of the bioavailability of divalent metals in sediment.
- Evaluate, quantitatively or qualitatively, the bioavailability of sediment associated COPCs using SEM:AVS or Equilibrium Partitioning approach.
- Compare the concentrations of PAHs that accumulated in worm tissues in the bioaccumulation bioassay to the no effect body residue (NEBR) that is associated with narcosis caused by PAHs and VOCs. Since all PAHs are assumed to act through the same mechanism of toxicity, the sum of all of the accumulated PAHs and VOCs is compared to the NEBR.
- Using sediment toxicity bioassays, determine which sediments at the Site have elevated toxicity to surrogates for resident macroinvertebrate species compared to sediments in reference areas.
- Determine on the basis of benthic macroinvertebrate sampling and analysis where benthic communities inhabiting sediments in waterbodies at the Site are impaired when compared to benthic communities inhabiting reference area sediment.

3.11.2.2 Assessment Endpoint #2: Viability and Function of Fish Community

The fish community_was selected as an assessment endpoint because of its significant role in lake energy flow, nutrient cycling and organic matter accumulation and because fish are an important food resource for higher trophic level species. This assessment endpoint will consider whether the sediment and surface water quality in aquatic potions of the Site are adequate to support a fish community composition and diversity that is within the range of natural variability of fish communities in Chequamegon Bay and to provide suitable forage for indigenous fish and wildlife species.

Risk Question:

Are concentrations of contaminants in sediments and surface waters of waterbodies at the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site surface water.
- Determine the concentrations of Site-related contaminants in tissue from fish caught in and adjacent to the Site.
- Compare concentrations of Site-related contaminants measured in Site surface water with toxicological benchmarks that have been associated with adverse effects to fish.
- Compare tissue levels of PAHs and estimated VOCs in wild fish caught at the Site to the NEBR.

- Using sediment bioassays, determine whether areas on and adjacent to the Site have elevated toxicity compared to sediment from reference areas to surrogates for juvenile resident fish species.
- Compare the concentrations of Site-related contaminants in tissue from fish caught at the Site to levels in fish from reference areas. (This assessment endpoint will be used only qualitatively as an indicator of exposure).

3.11.2.3 Assessment Endpoint #3: Viability and Function of Omnivorous Aquatic Bird Community

Omnivorous aquatic birds were selected as an assessment endpoint because they have an important role in energy transfer from the aquatic to the terrestrial ecosystem. Consumers of both aquatic plants and animals, they, in turn, provide an important food source for higher trophic levels. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity of omnivorous aquatic birds that is within the range of natural variability of omnivorous aquatic bird communities in other habitats in Lake Superior of this region.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?

Selected Receptor: Black Duck (*Anas rubripes*):

Black ducks are common at Site and breed in this part of Wisconsin. This bird's diet consists mainly of plant food (seeds, vegetative parts of aquatic plants and crop plants) and small aquatic animals including aquatic insects, molluscs, crustaceans and amphibians. They feed by grazing, probing, dabbling or upending in shallow water; occasionally they dive.

The feeding behavior of black duck, such as pulling up vegetation rooted in sediments, could result in exposure to Site-related contaminants in the sediment. They are small relative to other aquatic omnivorous birds such as geese and swans, and so have higher ingestion rates per unit body weight, yielding more conservative estimates of risk. Additional information on the life history of the black duck is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site sediment.
- Through food chain models for the black duck using sediment to benthic invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment. Restricting the model to a diet benthic invertebrates conservatively overestimates the dose expected when black ducks also ingest plant matter.

3.11.3 Terrestrial and Wetland Ecosystem

3.11.3.1 Assessment Endpoints #4 through #9: Viability and Function of the Terrestrial Vertebrate Community

The terrestrial vertebrate community is comprised of a variety of species that perform various roles within the terrestrial ecosystem. These roles include energy flow and organic matter production. Terrestrial vertebrates also serve as a link between the aquatic and terrestrial ecosystems on the Site.

Assessment Endpoint #4: Viability and Function of the Omnivorous Avian Community

Omnivorous birds were selected as an assessment endpoint because they consume plant and animal tissue from several different tropic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals. This assessment endpoint will consider whether surface water and soil quality is adequate to support a community composition and diversity of omnivorous birds that is within the range of natural variability of omnivorous bird communities in other terrestrial habitats in the region.

Risk Question:

Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?

Selected Receptor: Red-winged blackbird (*Agelaius phoeniceus*):

The red-winged blackbird is a seasonal resident of the Site area and feeds in both wetland and riparian areas. It feeds primarily on insects and weed seeds. Additional information on the life history of the red-winged blackbird is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site soils.
- Through food chain models for the red-winged blackbird using soil-to-vegetation and soil-to-invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Assessment Endpoint #5: Viability and Function of the Insectivorous Avian Community

Insectivorous birds were selected as an assessment endpoint because they consume insects from several different tropic levels and thus have an important role in energy transfer from insect tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity of insectivorous birds that is within the range of natural variability of insectivorous bird communities in other terrestrial habitats in the region.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous avian community?

Selected Receptor: Tree swallow (*Tacycineta bicolor*):

The tree swallow is a seasonal resident of the Site area and feeds primarily on flying insects in terrestrial, wetland and riparian areas. Many of these have been seen in the Site area during hatches of aquatic insects. Additional information on the life history of the tree swallow is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site sediments
- Through food chain models for the tree swallow using sediment-to-emergent aquatic insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Assessment Endpoint #6: Viability and Function of the Piscivorous Avian Community

Piscivorous birds have been selected as an assessment endpoint because they eat primarily fish and thus serve as an important pathway for nutrients and energy from the aquatic to the terrestrial ecosystem. They are also usually the highest trophic level in the food chain and would thus be potentially vulnerable to any contaminants that would bioaccumulate. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity of piscivorous birds that is within the range of natural variability of piscivorous bird communities in other terrestrial habitats in the region.

Risk Questions:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous avian community?

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse effects, including reproductive impairment, to individual ospreys.

Selected Receptors: Double-Crested Cormorant (*Phalacrocorax auritus*) and osprey (*Pandion haliaetus*):

The cormorant is a seasonal resident of the Site area and breeds locally. It is expected to feed primarily on small fish (4-8") as well as occasionally on amphibians. The osprey is a listed species (State threatened) that is expected to feed on small to medium sized fish (<12"). While the osprey has not been documented to use the Site, it is used as a representative species to provide a conservative exposure scenario for a listed piscivore. Additional information on the life history of the both species is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site sediments.

- Determine the concentrations of Site-related contaminants in fish caught in and adjacent to the Site.
- Through food chain models for the cormorant and osprey using actual levels of Site-related contaminants measured in fish, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Assessment Endpoint #7: Viability and Function of the Omnivorous Mammal Community

Omnivorous mammals were selected as an assessment endpoint because they consume plant and animal tissue from several different trophic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity that is within the range of natural variability of omnivorous mammal communities in other disturbed terrestrial habitats in the region.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the omnivorous mammal community?

Selected Receptor: White-footed mouse (*Peromyscus leucopus*):

The white-footed mouse is likely an abundant and permanent resident of the Site area and feed on seeds, berries, nuts and insects. Additional information on the life history of the white-footed mouse is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site soils.
- Through food chain models for the white-footed mouse using soil to plant and soil to invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Assessment Endpoint #8: Viability and Function of the Insectivorous Mammal Community

Insectivorous mammals were selected as an assessment endpoint because they consume insects from several different trophic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity of insectivorous mammals that is within the range of natural variability of insectivorous mammal communities in other terrestrial habitats in the region.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous community.

Selected Receptor: Big Brown Bat *(Eptesius fuscus)*

The big brown bat likely feeds in the vicinity of the Site. This bat is larger than the little brown bat and is a widespread species in North America. It roosts in colonies in tree hollows, wall spaces, and buildings. It is tolerant of cold conditions and may overwinter in walls and attics. It also hibernates in caves, abandoned mines, and sometimes in buildings. It feeds on a several types of flying insects. Additional information on the life history of the big brown bat is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in Site soils.
- Through food chain models for the small-footed bat using soil to insect and sediment to emergent aquatic insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Assessment Endpoint #9: Viability and Function of the Piscivorous Mammal Community

Piscivorous mammals have been selected as an assessment endpoint because they eat primarily fish and thus serve as an important pathway for nutrients and energy from the aquatic to the terrestrial ecosystem. They are usually the highest trophic level in the food chain and would thus be potentially vulnerable to any contaminants that would bioaccumulate. This assessment endpoint will consider whether surface water and sediment quality is adequate to support a community composition and diversity of piscivorous mammals that is within the range of natural variability of piscivorous mammal communities in other terrestrial habitats in the region

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?

Selected Receptor: Mink *(Mustela vison)*:

The mink is a permanent resident of the Site area where it feeds both on aquatic and terrestrial prey, the proportions depending upon the season. Although it is likely to be rare in the Site area because of the developed and disturbed nature of the habitat, the mink is used as an ROC because of its sensitivity and the availability of toxicological information. Additional information on the life history of the mink is found in Appendix F.

Measurement Endpoints (Exposure and Effects):

- Determine the concentrations of Site-related contaminants in fish caught in the Site area.
- Through food chain models using actual levels of Site-related contaminants measured in fish, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects.

3.11.4 Receptors of Concern

A BERA cannot specifically evaluate the potential for adverse effects to every plant, animal, and microbial species that may be present and potentially exposed in the Site area. As a result, receptors that are representative of high ecological or societal value, those believed to be representative of broader groups of organisms, or those potentially most exposed to Site contaminants were selected as "receptors of concern (ROC)" for evaluation in the BERA.

Each ROC was selected to reflect an assessment endpoint considering their trophic category and particular feeding behaviors (e.g., fish-eating birds versus insect-eating birds) that would represent different modes of exposure to COPCs. Consequently, the species that were chosen for evaluation may represent several similarly exposed species in the area.

The following criteria were used to select potential receptors:

- The receptor does or could use habitats that are present around the Site;
- The receptor is important to either the structure or function of the ecosystem;
- The receptor is statutorily protected (i.e., threatened or endangered species, migratory birds) or is otherwise highly valued by society (i.e., species of cultural importance);
- The receptor is reflective and representative of the assessment endpoints for the Site area; and,
- The receptor is known to be either sensitive or highly exposed to COPCs around the Site.

The soil invertebrate community was not selected as a ROC because the terrestrial portion of the Site is largely a developed urban area.

The species selected as ROCs are summarized by habitat type, and assessment endpoint level in Table 3-9. Life history profiles for each of the representative species are presented in Appendix F.

Table 3-9. Receptors of Concern.

ROC Category	ROC	Habitat
Aquatic Habitat		
Benthic macroinvertebrate community	Generic	Littoral portions of Chequamegon Bay
Fish Community	Generic	Littoral portions of Chequamegon Bay
Omnivorous birds	Black Duck	Littoral portions of Chequamegon Bay
Insectivorous birds	Tree swallow	Upland and riparian
Piscivorous birds	Double-crested cormorant Osprey (State endangered)	Littoral portions of Chequamegon Bay
Insectivorous mammals	Big brown bat	Upland and riparian
Piscivorous mammals	Mink	Upland and riparian
Terrestrial Habitat		
Omnivorous birds	Red-winged blackbird	Upland and riparian
Omnivorous mammals	White-footed mouse	Upland and riparian

As indicated in USEPA (1997), "Step 4 of the ecological risk assessment establishes the measurement endpoints [...], completing the conceptual model begun [earlier]. Step 4 also establishes the study design [...] and data quality objectives based upon statistical considerations." In this section of the Baseline Problem Formulation, the measurement endpoints, which were introduced in the last Section, are summarized and used to evaluate the assessment endpoints from Step 3 proposed.

4.1 PROPOSED MEASUREMENT ENDPOINTS AND DECISION CRITERIA

The measurement endpoints that will be used in this BERA are summarized in Table 4-1 with associated decision criteria. Data Quality Objectives for each assessment and measurement endpoint are discussed further in Section 4.2.

Table 4-1. Endpoints and Risk Questions.

Assessment Endpoint	Risk Question	Measurement Endpoint(s) (Exposure and Effects)
Benthic macroinvertebrate community	Are concentrations of contaminants at the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?	• Determine the concentrations of Site-related contaminants in Site sediment. • Determine the levels of TOC, soot, coal, coke and slag which may moderate the bioavailability of PAHs in the sediment. • Determine the levels of AVS:SEM in the sediment. • Compare concentrations of metals measured in Site sediment to WDNR (2003) sediment quality guidelines for TEC and PEC. • Evaluate, quantitatively or qualitatively, the bioavailability of sediment associated COPCs using SEM:AVS or Equilibrium Partitioning approach. • Compare concentrations of PAHs that accumulated in worm tissues in the bioaccumulation bioassay to the NEBR that is associated with narcosis caused by PAHs and VOCs. Use this as a model for predicting risk at the Site. • Using sediment toxicity bioassays, determine which sediments in and adjacent to the Site have elevated toxicity to surrogates for resident macroinvertebrate species compared

Table 4-1. Endpoints and Risk Questions.		
Assessment Endpoint	**Risk Question**	**Measurement Endpoint(s) (Exposure and Effects)**
		to sediments in reference areas. • Determine on the basis of benthic macroinvertebrate sampling and analysis where benthic communities inhabiting sediments in waterbodies in and adjacent to the Site are impaired when compared to benthic communities inhabiting reference area sediment.
Fish community	Are concentrations of contaminants in sediments and surface waters of waterbodies at the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?	• Determine the concentrations of Site-related contaminants in Site surface water. • Determine the concentrations of Site-related contaminants in tissue from fish caught in and adjacent to the Site. • Compare tissue levels of PAHs and estimated VOCs in wild fish caught at the Site to the NEBR. • Using sediment bioassays, determine whether areas on and adjacent to the Site have elevated toxicity compared to sediment from reference areas to surrogates for juvenile resident fish species. • Compare the concentrations of Site-related contaminants in tissue from fish caught in and adjacent to the Site to levels in fish from reference areas. (This assessment endpoint will be used only qualitatively as an indicator of exposure).
Omnivorous aquatic bird community	Are dietary exposure levels of Site-related contaminants sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?	• Determine the concentrations of Site-related contaminants in Site sediment. • Through food chain models for the black duck using sediment to benthic invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Table 4-1. Endpoints and Risk Questions.		
Assessment Endpoint	**Risk Question**	**Measurement Endpoint(s) (Exposure and Effects)**
Omnivorous birds	Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?	• Determine the concentrations of Site-related contaminants in Site soils. • Through food chain models for the red-winged blackbird using soil to vegetation and soil to invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Insectivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous avian community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Through food chain models for the tree swallow using sediment to emergent insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Piscivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to individual ospreys or to the piscivorous avian community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Determine the concentrations of Site-related contaminants in fish caught in and adjacent to the Site. • Through food chain models for the double-crested cormorant and the osprey using actual levels of Site-related contaminants measured in fish in and adjacent to the Site, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.

Table 4-1. Endpoints and Risk Questions.		
Assessment Endpoint	**Risk Question**	**Measurement Endpoint(s) (Exposure and Effects)**
Omnivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the omnivorous mammal community?	• Determine the concentrations of Site-related contaminants in Site soils. • Through food chain models for the white-footed mouse using soil to plant and soil to invertebrate bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Insectivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous mammal community?	• Determine the concentrations of Site-related contaminants in Site sediments. • Through food chain models for the big brown bat using sediment to emergent insect bioaccumulation factors, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects, including reproductive impairment.
Piscivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?	• Determine the concentrations of Site-related contaminants in fish caught in the Site area. • Through food chain models using actual levels of Site-related contaminants measured in fish, estimate the ingestion of Site-related contaminants and compare it to TRVs associated with adverse effects.

4.2 DATA QUALITY OBJECTIVES

4.2.1 The Data Quality Objectives (DQO) Process

The data quality objectives (DQO) process is described in USEPA guidance as "a seven-step planning approach to develop sampling designs for data collection activities that support decision making. This process uses systematic planning and statistical hypothesis testing to differentiate between two or more clearly defined alternatives". It is recommended by USEPA in RI/FS guidance (USEPA 1988) and ecological risk assessment guidance (USEPA 1997; 1998). The USEPA developed the DQO process "...as the Agency's recommended planning process when environmental data are used to select between two opposing conditions." A summary of the seven steps involved in the DQO process is presented in Table 4-2 below (from USEPA 2000)

Table 4-2.The Data Quality Objective Process.

DQO Step	Activity
Step 1. State the problem.	Define the problem; identify the planning team; examine budget and schedule.
Step 2. Identify the decision.	State decision; identify study questions; define alternative actions.
Step 3. Identify inputs to the decision.	Identify information needed for the decision (information sources, basis for Action Level, sampling/analysis method.)
Step 4. Define the boundaries of the study.	Specify sample characteristics; define spatial/temporal limits, units of decision making.
Step 5. Develop decision rule.	Define statistical parameter (mean, median); specify Action Level; develop logic for action.
Step 6. Specify tolerable limits on decision errors.	Set acceptable limits for decision errors relative to consequences (health effects, costs).
Step 7. Optimize the design for obtaining data.	Select resource-effective sampling and analysis plan that meets the performance criteria.

The goals of the DQO process are to:

- Clarify the study objective and define the most appropriate types of data to collect;
- Determine the most appropriate field conditions under which to collect the data; and,
- Specify acceptable levels of decision errors that will be used as the basis for establishing the quantity and quality of data needed to support risk management decisions.

4.2.2 Site Data Quality Objectives

DQOs have been prepared to ensure that data proposed for use in the risk assessment would be of sufficient quality, appropriate for the intended uses, and useful in meeting RI/FS objectives. The overall quality assurance (QA) objective of the project is to ensure that field and laboratory data collected during the RI has been precise, accurate, representative, comparable, and complete. Specific procedures for obtaining these QA objectives are presented in the Quality

Assurance Project Plans (QAPP) that accompanied the RI Work Plan and amendments. DQOs for the Site have included the following:

- Utilization of laboratory procedures and the appropriate analytical support (i.e. data validation) for identifying contamination consistent with the levels for remedial action objectives identified in the National Contingency Plan (NCP);
- Identification of the vertical and lateral extent of sediment, soil, surface water and groundwater contamination in the Site area;
- Utilization of historic and RI-generated site data to interpret geologic and hydrogeologic conditions with respect to evaluating contaminant migration pathways and the fate and transport of contaminants;
- Generation of laboratory data with appropriate detection limits to compare to media specific cleanup standards and to assess attainment of risk-based criteria;
- Utilization of historic and RI-generated data necessary to perform human health and ecological risk assessments;
- Utilization of historic and RI-generated data necessary to develop site-specific cleanup standards protective of human health and the environment; and
- Utilization of historic and RI-generated data for the evaluation of potential remedial alternatives that will achieve site-specific cleanup standards protective of human health and the environment.

A detailed discussion of these DQOs is presented in the Quality Assurance Project Plan (QAPP) that has accompanied the RI/FS work plan. Specific aspects of DQOs for the studies used to support this BERA are summarized in Appendix G, Tables 1-6.

4.2.3 Weight of Evidence Evaluation

As discussed in USEPA (1997),

> "Confidence in the conclusions of a risk assessment may be increased by using several lines of evidence to interpret and compare risk estimates. These lines of evidence may be derived from different sources or by different techniques relevant to adverse effects on the assessment end points, such as quotient estimates, modeling results, or field observational studies. There are three principal categories of factors for risk assessors to consider when evaluating lines of evidence: (1) adequacy and quality of data, (2) degree and type of uncertainty associated with the evidence, and (3) relationship of the evidence to the risk assessment questions [...]. Data quality directly influences how confident risk assessors can be in the results of a study and conclusions they may draw from it. Specific concerns to consider for individual lines of evidence include whether the experimental design was appropriate for the questions posed in a particular study and whether data quality objectives were clear and adhered to. An evaluation of the scientific understanding of natural variability in the attributes of the ecological entities under consideration is important in determining whether there were sufficient data to satisfy the analyses chosen and to determine if the analyses were sufficiently sensitive and robust to identify stressor caused perturbations. Directly related to data quality issues is the evaluation of the relative uncertainties of each line of evidence [...]."

Weighting of evidence should be used for two purposes:

1) Weighting of the value of the various measures or studies that are used to support a line of evidence, e.g., deciding which toxicological study is the most relevant in deriving a toxicological benchmark for use at a specific site; and,
2) Weighting of relative value of each line of evidence in determining what estimate of risk is most likely for site receptors given the results from that line of evidence.

The process of weighing various measures and studies or the relative value of each line of evidence may consider such factors as:

1) Relevance of the study to the assessment endpoint;
2) Strength of the exposure-response relationship;
3) Appropriateness of the study temporal scope;
4) Appropriateness of the study spatial scope;
5) Quantity of data; and,
6) Quality of data.

The lines of evidence used in this BERA will be accorded the following weight of evidence [numbered according to relative significance, with 1) having greater weight than 3)]:

1) Comparison of observed effects in the receptor group community characteristics in waterbodies in and adjacent to the Site to receptor group community characteristics from reference areas;
2) The results of bioassays conducted using standardized toxicity tests with sediments in and adjacent to the Site and surrogate test organisms;
3) Comparison of site-specific media concentrations and/or estimated ingested contaminant dose estimates (the latter for wildlife) to effects levels [(toxicological benchmarks and TRVs][6] for the various ROCs.

Not all lines of evidence are necessarily used for each receptor group but when multiple lines of evidence are used the highest weight, i.e. the most important, should be accorded the results of site-specific studies. For instance, if there are conflicting results from the various lines of evidence, results from site-specific studies, e.g., from sediment bioassays using sediment from the Site or comparison of the tissue residue levels of organisms collected at the Site to tissue residue levels from similar species in reference areas, should be deemed more reliable for evaluating potential risk, then comparison to TRVs for surrogate species. To the extent that additional lines of evidence are used for any of the assessment endpoints, it is recommended that a process be employed to reach consensus on the relative weight of evidence for these lines. As an example, if adequate information is available, the Triad approach offers the benefit of precedent in interpreting multiple lines of evidence relating to sediment quality.

[6] In this risk assessment the term "Toxicological Reference Value" will be used for effects levels for birds and mammals, while "toxicological benchmark" will be used for effects levels for other receptors.

For those lines of evidence where Hazard Quotients (HQs) were calculated, the risk questions presented in Section 3.9.1 and Table 4-1 will be answered in the affirmative if the hazard quotient was greater than one.

During the analysis phase, an evaluation of ecological and chemical data is conducted to determine the potential for ecological exposure and adverse effects. The management goals and objectives, assessment endpoints, and measures of effect, as well as the ecological CSM developed during problem formulation help focus this analysis. The analysis consists of two components: (1) effects analysis and (2) exposure analysis. These two components are used to evaluate the relationships between receptors, potential exposures, and potential effects. The results of these evaluations provide the information necessary to estimate potential risks to the representative species.

5.1 EFFECTS ANALYSIS

The Effects Analysis consists of an evaluation of available toxicity or other effects information that can be used to relate the exposure estimates to a level of adverse effects. Stressor-response (i.e., effects) data that are used to evaluate ecological risks in this BERA are of three types: (1) literature-derived toxicity data, (2) site-specific ambient media toxicity tests (e.g. sediment toxicity tests), and (3) site-specific biological community surveys.

The focus of majority of the effort for this BERA was on aquatic portions of the Site. For the evaluation of Site sediment all three lines of evidence were integrated into a Sediment Quality Triad (Triad) (Long and Chapman 1985; Chapman et al. 1987). The Triad evaluates sediment quality by integrating spatially and temporally matched sediment chemistry, biological, and toxicological information. Benthic invertebrate community analysis and sediment toxicity testing provide site-specific information regarding potential ecological effects of exposure of ecological receptors to COPCs in the Site sediment. These additional lines of evidence supplement traditional bulk sediment chemistry data to provide a more relevant, site-specific assessment of risks.

The evaluation of bulk sediment chemistry data involves comparison of Site sediment chemistry data to effects levels derived from relevant studies reported in published literature or performed for this BERA. These data may also be represented as generic criteria or guidelines that have been developed from toxicity data, e.g., National Recommended Water Quality Criteria (NRWQC). Toxicity data developed for use in this BERA are summarized in this Section and the details are presented in Appendix H. Site-specific sediment toxicity tests also have been conducted with aquatic receptors that are representative surrogates for those living on the Site. This testing provides information on potential toxic effects that were observed in Site relevant organisms exposed to Site sediment. The results of the sediment toxicity testing done for this Site are summarized in this section and Site-specific sediment toxicity test reports are presented in Appendix B. Site-specific surveys of benthic macroinvertebrate community also were conducted for the Site. A summary of this investigation is presented in this section and Appendix B provides further details.

In addition to these three lines of evidence for aquatic portions of the Site, surface water quality data and fish tissue data were collected from Site waters.

For upland portions of the Site only two lines of evidence were used in this BERA. One was the comparison of bulk soil chemistry to soil quality benchmarks used as generic criteria, e.g., the soil ECO-SSLs (USEPA 2005a) or derived from relevant studies reported in published literature. The second is the comparison of doses accumulated through the food chain that terrestrial and aquatic prey-dependent wildlife (i.e., birds and mammals) may feed upon. These doses were compared to toxicity reference values derived from the primary scientific literature.

The result of this ecological effects analysis is a range of TRVs that will be compared with the dose estimates (birds and mammals) or toxicological benchmarks that will be compared with estimated exposure point concentrations (EPCs) (benthic invertebrates and fish) to estimate potential risks in this risk characterization.

5.1.1 Site Contaminants of Concern

While the primary Site COPCs are derived from tar related to historical industrial operations at the Site, there are other COPCs whose origin is uncertain. Tars contain a number of non-toxic and potentially toxic chemicals. By far the greatest percentage of tar components are non-toxic because they are not water soluble or bioaccessible. The toxicity of tars is due largely to the aromatic hydrocarbons and, to a lesser degree, the short-chain alkanes, phenols, and other components such as cyanide and ammonia. The tar related COPCs for this Site include VOCs, principally BTEX, and SVOCs, principally PAHs. Of these, the PAHs are considered the most potentially bioaccessible and toxic. Therefore, PAHs are considered the major source of toxicity at the Site and are the focus of this ecological risk assessment.

As discussed in Section 3.6 in addition to tar associated COPCs, the levels of some other chemicals were higher than the screening values for sediment and soil quality and also will be addressed in this Effects Analysis. These included barium, copper, selenium and thallium in sediment and antimony, cadmium, lead, manganese, mercury, selenium and zinc in soil. No COPCs were identified in surface water samples.

These other COPCs likely originated from the various industrial operations that occurred on this Site (See Section 2.2) or may have originated in the backfill.

Based upon comments by USEPA, screening to determine COPCs was conducted based upon comparison of the maximum detected concentration to the screening criteria. However, USEPA also indicated that use of the UCL_{95} was appropriate for quantifying intake and characterizing risks. Section 5.2 provides a list of the COPCs for which TRVs will be developed in this section.

5.1.1.1 Tar Related Compounds

Tar is a complex mixture of hydrocarbons which may be divided into at least four operationally-defined major categories:

1) Aromatics;
2) Saturates;
3) Resins; and
4) Asphaltenes.

Aromatic hydrocarbons (AHs) are compounds sharing the cyclic unsaturated bonds (π bonds) found in benzene. AHs are further characterized according to the number of benzyl rings (e.g., naphthalenes are di-aromatic, anthracene is tri-aromatic, and pyrene is tetra-aromatic). Aromatics may also be classified as mono- -(i.e., often called VOCs) and poly (polycyclic) aromatic (PAHs). PAHs are further subdivided into low molecular weight (LMW) or high molecular weight (HMW) PAHs. VOCs are volatile and relatively water-soluble, but are also relatively non-toxic to aquatic organisms. The LMW PAHs are less water-soluble and bioaccessible[7] than VOCs, but are more toxic. HMW PAHs are even less water-soluble and bioaccessible but are potentially the most toxic members of this group of tar compounds. In tars, the aromatic hydrocarbons mostly belong to the benzene, naphthalene, anthracene, and phenanthrene series. Naphthalene, a LMW PAH, is often the largest single component of unrefined, un-weathered, tar, with concentrations of between 7 and 12%. Although PAHs are mostly comprised of carbon and hydrogen atoms, sulfur, oxygen, and nitrogen may substitute for carbon to form heterocycles. VOCs usually comprise a small portion of the total aromatics of tars and this portion decreases as tar environmentally "weathers" with age due to their volatility and leaching by water. VOCs made up about 3% of the total AHs in some Site sediments. In soil, VOCs were less than 2% of the total AHs.

Saturates are non-polar aliphatics comprised of straight-chain, branched, and cycloalkanes (naphthenes) hydrocarbons. Short-chain alkanes are highly water-soluble saturates but are also highly volatile and non-persistent. The paraffins (waxes) are long, straight-chain alkanes that are very water-insoluble.

Resins are operationally defined as the portion of tar that is insoluble in propane, but soluble in pentane or heptane. Resins are polar molecules often containing heteroatoms, atoms other than carbon in the structure of a heterocyclic compound. Resins are structurally similar to asphaltenes but have lower molecular weight. Resins are also insoluble in water.

Asphaltenes are very HMW aromatics that are operationally defined as the fraction of tar that precipitates in pentane, hexane or heptane, but not in toluene or benzene. Asphaltenes contain the largest number of heteroatoms and organometallic constituents. The molecular weights of asphaltenes are difficult to assess, but are believed to range fro 500 to 2,000 g/mole. Asphaltenes are insoluble in water.

Besides the hydrocarbons, tars may include about 2% of the simpler phenols, the best known of which is carbolic acid. The phenols are highly soluble in water. Trace minerals found in the coal (arsenic, chromium, lead, etc.), as well as cyanides, sulfur, and ammonia are other potentially toxic components of tars. The actual composition of the individual tar components is highly dependent on the coal source, method used to make the coal gas, and the degree of exposure to oxidizing conditions (i.e., weathering).

5.1.1.2 PAHs in Site Sediments

As discussed in Section 2.0 contamination in Site sediments is mainly confined to a sediment layer extending a few hundred feet from the shoreline. This contaminated sediment layer is thickest near the shoreline, typically 3 to 4 ft, and tapers off in the offshore direction. The areas

[7]Bioaccessibility refers to the portion of the diet that is desorbed from the food or soil and is dissolved in the stomach or gut contents. For a chemical to be bioavailable it has to be both bioaccessible and assimilated across the gut epithelium. Therefore, the bioaccessible portion is a conservative estimate of the bioavailable portion. Because of precedent the term bioavailability will be used as the inclusive term for both elements of bioavailability in the following discussion.

with the highest levels of contamination tend to mimic the shape of the shoreline. Layers of wood mulch are sometimes found overlying or within the contaminated sediment layer. The wood mulch layer varies in thickness from 0 to 6 ft, averaging about 9 inches across the Site. It is estimated that approximately 25,000 cubic yards of wood mulch are found in the nearshore area, and most of this overlies the sediment bed (URS 2006b). Native sediments underlying the wood mulch layer consist of interbedded layers of sand, silty sand, silt and silty clay. The highest concentrations of VOCs and PAHs were detected in sediment samples collected in the area south of a line between the former WWTP and the marina, an area north of the former WWTP, and in the area between the former WWTP and the boat launch. The highest concentrations are found at sediment depths between 0 and 6 ft (URS 2001).

Newfields (2005) conducted a forensic analysis of the soils and sediments from the Site. They concluded that sediments at stations closer to shore had a composition of PAHs similar to that found in soils at the Tar Dump. The hydrocarbon composition at stations further offshore was more similar to regional background sediments and soils at Kreher Park. Both samples also contained modern organics and degraded vegetative debris. Higher concentrations of PAHs and soot were also found at the stations closer to shore.

As discussed further below, the presence of wood mulch and soot modify the bioavailability and bioaccessibility and, therefore, the toxicity of PAHs.

Bioavailability of PAHs in Sediments

In order to make contact with or enter an organism, chemicals must be bioaccessible. The bioaccessibility of PAHs is governed by the balance between their affinity for like substances, such as organic carbon or dense non aqueous phase liquid (DNAPL), and their aversion to unlike substances, such as water. This affinity is most frequently described as the octanol-water partition coefficient, or Kow. HMW PAHs also have a relatively high Kow, while LMW PAHs have a relatively low Kow. The most commonly measured organic carbon sources to which PAH bioaccessibility is correlated are total organic carbon (TOC) in the bulk sediment (and soil) and dissolved organic carbon (DOC) in the sediment or soil porewater. As the concentration of TOC and/or DOC increases, the bioaccessibility of PAHs decreases, although this is more important for HMW than LMW PAHs. At the Site, the most obvious form of organic matter is wood mulch, and, as discussed later, areas of wood mulch have been associated with lower levels of toxicity in sediment bioassays at the Site.

In addition to wood mulch another source of organic carbon in site sediments is soot. Soot made up as much as 10% of the sediment at some of the sediment stations (Table 5, Newfields 2005). When hydrocarbons are exposed to high temperatures, but without sufficient oxygen to allow complete combustion, they polymerize to form soot. Because soot is composed of hydrocarbons, PAHs are attracted and tightly bound to soot. Studies have shown that binding to soot is tighter than to TOC (Lamoureux and Brownawell 2004) which results in lower bioaccessibility than predicted by equilibrium partitioning (Accardi-Dey and Gschwend 2003; Sunderlin et al. 2004; Rust et al. 2004). The other potential organic carbon source in sediments at the Site is coal and coal dust from various sources in the vicinity of the Site. However, based upon petrologic analysis of site sediments other than Station SQT8, where coke and coal made up 6% of the sediments, coal (or coke) was not found in any quantity in Site sediments (Newfields 2005).

Effects of Weathering on the Bioavailability of PAHs

When tars are exposed to sunlight and water their composition is changed. Contact with water removes the more water-soluble LMW PAHs by dissolution and photo-oxidation changes the PAHs to other, more water-soluble forms such as acids, alcohols, ketones, aldehydes and quinones (Ehrhardt and Burns 1993). In both cases, these water-soluble products are diluted in the surrounding water and only very low concentrations have ever been measured. Weathering is likely to be a very important factor influencing potential toxicity because LMW PAHs and other water-soluble components volatilize or leach from sediments. The remaining tar products will, therefore, be relatively enriched in HMW PAHs and water-insoluble components. As discussed below, there is a large difference in the toxicity of LMW and HMW PAHs.

Photo-oxidation occurs due to short wave length UVA (320-400 nm) and UVB (280-320 nm) light. Photo-oxidation preferentially depletes alkyl-substituted PAHs and heterocyclic PAHs (Ehrhardt et al. 1992). Some of these oxidation products may be more toxic than the parent compounds. However, because only a small fraction of the total volume of tar is weathered, the concentration of the oxidation products is small. In fact, Ali et al. (1995) reported that under controlled laboratory conditions, only 12% of phenanthrene was found as photoproducts after 7-hrs exposure to intense UV light. Furthermore, in sediments contaminated with crude oil, Ehrhardt and Burns (1993) reported photo-oxidation products in water samples, but not in sediments because the products were water-soluble and leached from the sediments. Furthermore, despite the heavily weathered condition of these sediments, the concentrations of these products in infaunal benthic invertebrates were lower than those of the parent compounds. Because only the LMW PAHs are water-soluble and bioaccessible, the composition of parent PAHs in infaunal benthic invertebrates is biased towards the lighter fraction. Further degradation follows since the water-soluble products are readily consumed by microbes as a carbon source.

5.1.2 Mechanisms of Toxicity of PAHs to Aquatic Organisms

It is generally accepted that PAHs cause toxicity to aquatic organisms primarily by narcosis (DiToro et al. 2000; Swartz et al. 1995; Russom et al. 1997; Barron 2000; McGrath et al. 2004). Narcosis is a nonspecific, reversible, disruption of neural activity (i.e., anaesthesia).

There are currently two theories about how narcosis works. The "critical volume theory" involves the disruption of nervous conductance caused by changes in the nerve cell membrane lipid composition due to the accumulation of toxicant molecules. The "protein binding theory" involves the interaction of toxicant molecules with specific receptors in or on the nerve cell. In either case, a certain constant molar volume of narcotic chemicals must be reached in order to cause the effect. For instance, several small molecules that occupy the space of a single large molecule will cause the same degree of narcosis. This has been shown in studies by Protic and Sabljic (1989) and Mortimer and Connell (1995) using various non-polar organic chemicals. Furthermore, since AHs exhibit the same quantitative structure-activity relationships (QSARs) between toxicity and the potential for uptake of other classical non-polar narcotics, and because the toxicity of PAHs and VOCs is additive on a molar basis (Landrum et al. 1991), it can be assumed that all PAHs and VOCs are also narcotics.

However, narcosis may not be the sole cause of toxicity to certain fish species. This is because, although all fish can detoxify PAHs through metabolism, certain fish may metabolize certain PAHs to metabolites that can cause cancer in the fish. Cancer does not occur in aquatic invertebrates, either because their life times are too short for cancer to develop, or because they do not produce these metabolites. However, as discussed below, the field data for PAHs as the cause for cancer in fish is controversial because there are numerous carcinogens in the aquatic environment and only certain species appear to be susceptible. Therefore, it is important to understand the metabolism of PAHs by fish, and the relative rates of detoxification vs. the formation of carcinogenic metabolites. This subject is discussed more extensively in the following sections.

PAH Metabolism by Aquatic Organisms

Once PAHs are dissolved in water they are subject to metabolism both within microbes and within higher organisms. Within most higher animals, PAHs are metabolized by the cytochrome P450-dependent (CYP1A1) Phase 1 enzyme system to products that are more water-soluble and may have much more specific mechanisms of toxicity than narcosis. The degree of metabolism depends in large part on phylogeny, with more advanced animals being more capable of metabolism than less advanced animals. Because the metabolites produced are more water-soluble, they are more easily released from the body than the parent compound (active excretion plus passive diffusion).

However, it is not clear that metabolism of PAHs is uniformly beneficial, since certain metabolites appear to be more toxic than the parent. Since metabolic capacity is lower in animals such as invertebrates and fish than in mammals, there appears to be a trade-off between the creation of a small mass of more toxic metabolites, and the high mass of the less toxic parent compound. For instance, Landrum and Scavia (1982) reported that the amphipod, *Hyalella azteca*, metabolized only about 2.1% of an anthracene body burden per hour, and Landrum (1988) and Landrum et al. (1994) reported no metabolism of a series of PAHs by the amphipod, *Diporeia spp.* (formerly *Pontoporeia hoyi*). Since very few or no toxic metabolites are formed, any adverse effects must be due to narcosis in these organisms.

On the other hand, in higher animals, where metabolism is faster, more toxic metabolites are produced at a higher rate and these have been associated with oxidative damage (i.e., free radicals) and carcinogenesis.

Even in animals that form more toxic metabolites, these may be further metabolized and detoxified by the Phase II system of epoxide hydrolases and glutathione S-transferases. In fact, even under acute exposure conditions, PAHs are generally not detected in fish tissue, unless in the presence of a continuing source of LMW PAHS to the water column or items in the fish diet, and exposure can only be shown by the measurement of conjugated metabolites in the bile. The uptake of PAHs by fish is determined by the affinity of PAHs for lipids in fish tissues and this affinity increases as Kow increases. Therefore, if PAHs are bioavailable for uptake to fish, i.e. in the water column and diet, HMW PAHs are theoretically more likely to be accumulated than LMW PAHs in fish tissue. However, since the uptake is relatively slow, PAHs are frequently not detected because the rate of metabolism equals that of uptake. Furthermore, fish metabolize HMW PAHs with greater efficiency than LMW PAHs.

Exposure of fish to sublethal concentrations of PAHs can activate the CYP1A1 gene so that PAHs are more rapidly metabolized. This phenomenon is called induction. Induction results in an increase in tolerance such that fish can survive concentrations of PAHs that are toxic to PAH-naïve fish. For instance, Diamond et al. (1995) reported that fathead minnows exposed to a sublethal level of fluoranthene increased their tolerance to PAHs by 30%. This is good evidence that the primary mechanism of toxicity of PAHs is narcosis rather than oxidative damage and that any metabolites produced are less toxic than the parent. As a result of induction, wild fish chronically exposed to sublethal levels of PAHs in the field would be expected to be more tolerant of PAH exposure than naïve fish tested in the laboratory.

The metabolism of PAHs not only produces metabolites, but also free radicals that can react directly with biological molecules. Such free radicals can cause cellular injury when they react with proteins or lipids or can be detoxified when they react with antioxidants such as ascorbate or carotenes. This antioxidant system is normally capable of detoxifying radicals created by normal metabolism and some degree of toxicant-induced radical generation Over time resistant animals appear to be selected under such exposure conditions such that populations remain stable. However, under high exposure conditions both the Phase I and Phase II systems can be overwhelmed.

Even when the Phase I, Phase II, and antioxidant systems perform perfectly, some PAH metabolites could potentially react with cellular components to cause sublethal adverse effects. These effects range from individual cell swelling (cytomegaly), to cell death (necrosis). Certain HMW PAHs that contain a "Bay" region may be metabolized to highly reactive epoxide intermediates capable of binding to DNA and causing mutations. These mutations occur at oncogenes, such as the Ki-*ras* oncogene[8]. Under normal conditions, these mutated cells are recognized by the cellular immune system and killed, but some of these cells escape detection and may go on to replicate themselves. Cell replication is stimulated when cell injury is present, and when PAHs cause cell injury they may stimulate the replication of normal as well as "transformed" cells. Over time, the replication of genetically transformed cells may result in cancer.

However, malignant cancer is a disease that requires an accumulation of genetic alterations. Most tumor cells are genetically unstable, as manifested by the genomic heterogeneity between cells within a tumor. This genetic instability may accelerate tumor progression by promoting mutations that convey a growth advantage. The increase in mutation frequency in cancer cells may be explained by the inactivation of genes involved in maintaining the integrity of the genome. These include the p53 tumor suppressor gene, the mismatch repair genes, and genes involved in controlling replication during mitosis. Oncogenes are expressed in tumors from fish (Goodwin and Grizzle 1994), but no corresponding point mutations, at least in the Ki-*ras* oncogene, have been found (Peck-Miller et al. 1998. During periods of stress and old age, when the immune system is sub-optimal, the incidence of tumors is increased. Chemical stress from many different sources may suppress the tumor suppressor gene P53. Thus, old, immune

[8]Oncogenes are genes that have sequences that are susceptible to mutation and are frequently found to be modified in cancer cells. Ki-ras is a particular sequence that is similar to that found in retroviruses and is found in cancer cells.

suppressed fish and PAH-exposed fish have both been shown to have elevated levels of liver tumors.

Certain naturally occurring chemicals also reduce cancer incidence in fish. Reddy et al. (1999) showed that chlorophyllin reduced the incidence of carcinogenesis in rainbow trout that were fed dibenzo[a,l]pyrene, and that this effect was not simply due to a reduction in bioaccessibility through complexation.

In summary, fish possess multiple levels of detoxifying mechanisms, and detoxification is the major fate for PAHs. The field data for PAHs as the cause for cancer in fish is controversial because there are numerous carcinogens in the aquatic environment and only certain species appear to be susceptible. Cancer is not an endpoint for invertebrates since they neither produce carcinogenic metabolites or live long enough to develop cancer.

Relative Metabolite Yield in Fish

The cytochrome P-450 system in fish is primarily a detoxification system, and most of the metabolites formed from PAHs are less toxic than the original parent compound. Although the focus of much of the research into the metabolism of PAHs is on negative effects including carcinogenesis due to some metabolites, few studies have reported the relative yield of PAH detoxified metabolites relative to the potentially carcinogenic metabolites. However, the fact that PAH metabolites are routinely measured in bile but are non-detectable in liver and flesh suggests that most PAHs are efficiently metabolized, conjugated, and excreted as non-toxic compounds. Balk et al. (1984) exposed pike larvae to [^{3}H]BaP in the diet and in the water. When fed, the pike initially (1.3 days) accumulated benzo(a)pyrene (BaP) in the liver and kidney, but by day three the liver, gall bladder, intestine and rectum continued to concentrate radioactivity. By day 21, the liver and kidney radioactivity had decreased. When exposed in the water, the gills and skin initially accumulated BaP, but the liver, bile duct, kidney and bladder were also labelled between 12-h and 3 days. Between 3 and 21-days, the intestine and rectum became labelled, presumably as the result of biliary excretion. The gall bladder contained over 50% of the radiolabel between day 1 and day 8.5. The highest percentage reached by the liver was 18% on day 14 and this was reduced to 4.8% by day 23. At day 23, the gall bladder accounted for 28% and the intestine 38%. This indicates that BaP was metabolized and excreted into the bile and urine, and that, at most, <5% could have remained bound to the liver tissue. The virtual absence of radiolabel from adipose tissues shows that only PAH metabolites were available for distribution to the other tissues. This shows that most parent PAH was cleared from the body and that very little remained to cause adverse effects.

Studies with wild fish have also shown that the majority of metabolic products of PAHs are benign. Among wild freshwater fish, Baumann et al. (1996) have shown that brown bullhead appear to be the most sensitive to chemically-induced carcinogenesis. Steward et al. (1990) evaluated the distribution and composition of BaP administered to brown bullhead. They reported that the highest concentrations of BaP were found in the bile and consisted of 10% unmetabolized BaP, and 81% water-soluble metabolites which are excreted. The potentially genotoxic metabolite BP-7.8-dihydrodiol accounted for only 3% of the total radioactivity in the bile. In addition, the results from the brown bullhead cannot be extrapolated to other species of freshwater fish. Willett et al. (2000) reported that both brown bullhead and channel catfish produce more non-toxic BaP-diones than the proximal carcinogenic 7,8-dihydrodiols.

Furthermore, the channel catfish clears PAHs more rapidly than brown bullhead and does not produce mutagenic PAH metabolites. This is due to channel catfish having greater activities of the Phase II detoxification enzymes and being able to detoxify and eliminate PAHs more efficiently than brown bullhead.

Similar in-depth studies are not available for salmonids, perhaps because this class of fishes are relatively primitive and may not produce the yield of metabolites necessary for analysis. When trout were exposed to between 1.2 and 4.0 µg BaP/L for 30-days, no hepatic DNA adducts were formed (Potter et al. 1994) and when BaP was administered by i.p., only 2.38% of the administered dose was recovered as hepatic DNA adducts (Schnitz and O'Connor 1992). Presumably, the remaining 97.6% did not form metabolites that bind to DNA. From these studies it appears that the brown bullhead studies represent the worst case for carcinogenesis in freshwater fish and the characteristics of this species should not be generalized to the other species that frequent the Site.

In summary, although carcinogenic metabolites may be formed by certain fish species, detoxification is the more likely fate for PAHs.

<u>*Evidence for PAH-Induced Carcinogenesis in Fish*</u>

Whether or not the mechanisms discussed above are a significant source of biological effects in the environment is still open to question. Although numerous studies have produced tumors in fish in the laboratory, few controlled few studies have produced tumors using PAHs, and none were identified that used environmentally-relevant concentrations.

Hawkins et al. (1990) exposed Japanese medaka and guppies to 30-250 µg BaP and or 7,12-dimethylbenzo(a) anthracene/L and reported liver tumors. However, these concentrations were only obtained by using dimethylforamide as a solvent to achieve adequate aqueous solubility. Hendricks et al. (1985) fed rainbow trout a diet containing 1000 µg BaP/kg for 18-months and reported liver tumors.

Although carcinogenesis has been produced in several species of fish in the laboratory, it has only been reported in some species of bottom-feeding in the wild. Even within an apparently similar feeding guild (fish with the same feeding ecology), large interspecies differences have been described. For instance, Malins et al. (1987) showed that within the same creosote-impacted harbor, two marine species of bottom-dwelling flatfish have drastically different incidences of liver tumor. English sole had a hepatic carcinoma incidence of 45% while starry flounder had an incidence of <1%. Similarly, there are numerous reports of hepatic of tumors in brown bullhead, but none in the closely related channel catfish. Furthermore, tumors have never been found in wild salmonids even though they can be induced in the laboratory (Hendricks et al. 1985).

Baumann and Harshbarger (1995) reported sediment and whole body PAH concentrations and incidences of hepatic lesions, including hepatocarcinoma, in brown bullhead at an industrial site in Ohio. In 1982, the sediment PAH[9] concentration was 381 mg PAH/kg, the whole fish

[9] Total PAH concentrations are dependent on the number of PAHs analysed. In 1982, only 11 PAHs were analysed; while 44 PAHs were analysed in 2000.

concentration was 0.48 mg PAH/kg (wet weight), and the incidence of cancer was between 31.2 and 41.1%, depending on age class. When sediment concentrations decreased to 4.3 mg PAH/kg, cancer incidence decreased to between 2.1 and 10%, again, depending on age class. Pinkney et al. (2004) reported liver tumors in between 50 and 68% of brown bullhead in the Anacostia River (MD) where the different surveys have reported mean sediment PAH concentrations of 26.8, 77.3, and 249 mg/kg. Although these concentrations of PAHs are lower than those studied by Baumann and Harshbarger (1995), the percentage of bullhead in the Anacostia with hepatic tumors is greater than the highest reported incidence in the Great Lakes.

This high variability of effects of PAHs on fish may be because PAHs are not the only, or the most potent, organic chemicals in sediments capable of causing carcinogenesis. High incidences of liver tumors have also been found in areas where low concentrations of PAHs were found in the sediments. Barron et al. (2000) reported an increased incidence of hepatic tumors in walleye from Green Bay, WI, but attributed these lesions to the presence of PCBs in sediments. Mikaelian et al. (2002) also reported hepatic tumors in whitefish that were associated with PCBs, chlorobenzenes and pesticides, but not PAHs. Black et al. (1982) reported nearly 100% hepatocarcinoma in sauger and 5-10% hepatocarcinomas in walleye from Torch Lake and Keweenaw Waterway, MI, where copper was the only contaminant identified. The high incidence of hepatic parasitism in sauger also may have contributed to the high levels of tumors because liver injury stimulates cell replication of both normal and transformed cells. High incidences of epidermal hyperplasia and dermal sarcomas found in walleye in Oneida Lake were shown to be caused by retroviruses. It is possible that the common denominator in all of these studies is not the presence of reactive metabolites, but the generation of reactive oxygen free radicals (Greenberg 2005), generated by reactions to PAHs, PCBs, lipids, metals, or cellular reactions to parasites i.e., leukocytes).

5.1.2.1 Phototoxicity of PAHs in the Aquatic Environment

Ultraviolet Light

There is a body of literature, based largely on laboratory experiments, that indicates that some PAHs when incorporated into the bodies of aquatic organisms, can become more toxic to the organism when the organisms are exposed to ultraviolet light (UV). UV light is the highest energy light reaching the Earth's surface. UV light is a normal component of sunlight, but it is invisible to the human eye. UV light has been divided into three subunits according to their wavelengths, UVA (320-400 nm), UVB (280-320 nm) and UVC (200-280 nm). About 90% of the total UV sunlight reaching the earth is UVA and the rest is UVB. Many atmospheric gases (i.e., ozone) and aerosols (i.e., water) selectively absorb UVB and reduce its penetration to the earth's surface. UVC is completely absorbed and does not reach the Earth. Of the wavelengths reaching the earth's surface, UVB is the most dangerous to aquatic life.

UVB and UVA penetrate surface waters to a depth that varies with site-specific absorbing capacity. The UV penetration can vary from a few centimeters to tens of meters depending on water transparency and time of year. However, the UVB portion of the spectra is absorbed to a greater extent than the UVA portion, even in pure water. This results in a reduction of the most damaging UV energy reaching aquatic organisms under natural conditions.

As the sun rises and sets the angle of the sun and the spectra of wavelengths that reach the earth's surface also changes. This is due to the longer light path through atmospheric ozone and particulates during the morning and evening, and, within water bodies, the back-scattering of light from reflective surfaces. As a result, to accurately reproduce the effects of UV light in the laboratory it is essential to record changes in the UV spectrum from dawn to dusk and to integrate the area under the curve in terms of energy.

Biological Effects of UVB Light

As discussed above, UV light is divided into UVA, UVB, and UVC. However, it is thought that UVB, or near UVB wavelengths, because of their higher energy relative to UVA or UVC, can directly cause the most adverse effects on organisms. The primary target of UV injury is generally considered to be DNA, but other studies have cited effects on external organs such as gills as other important targets. Most studies have reported that although UVA is more abundant, it is UVB that is responsible for cellular injury. For instance, Williamson et al. (2001) reported that 320 nm (UVB) is 110-fold more damaging to *Daphnia magna* than that caused at 370 nm (UVA).

A dose of UV light is like any other toxicant in that the critical factors are the concentration and duration of exposure. In the case of UV light, the concentration is the exposure energy, commonly expressed as $\mu W/cm^2$. However, the toxicity of UV light has been assumed by many researchers to be governed by the reciprocity principle. The reciprocity principle states that a given total dose of radiation is independent of exposure duration. Therefore, the same effect is found for short, high-energy doses as for long, low-energy doses, so long as the dose (energy x duration) is the same. For organisms that do not have well-developed photoenzymatic repair (PER) mechanisms, reciprocity works as expected. However, for organisms with PER capacity, UV-induced toxicity acts like chemically-induced toxicity in that tolerance is a balance between the rate of injury and the rate of repair.

In both chemical and UVB-induced toxicity, the ability to repair injury can be overwhelmed by short-term high intensity exposures, even if the total exposure is equal to a long-term no effect exposure. The PER mechanism to repair DNA depends on the enzyme photolyase which reverses the cross-linking between adjacent DNA strands formed by UV energy. This reaction is of interest because it occurs only in the presence of UVA and visible light. This is one reason why laboratory experiments that do not replicate field conditions in terms of exposure spectra (i.e., UVA and visible light) and duration (i.e., 8-hours darkness) cannot be extrapolated to field conditions.

Modifying Factors and Adaptations to UV Light in the Aquatic Environment

In some clear lakes in North America, 99% of UVB reaches a depth of only 4 m while 99% of UVA reaches a depth of 10 m. However, in the water column of most lakes, dissolved (DOM) and particulate organic matter (POM) reduce UV penetration by absorbing the UV energy. DOM comprises a complex array of carbon containing compounds derived from the decomposition of dead organisms. Offshore, the major portion of POM is phytoplankton, but nearshore, where wave action keeps sediment suspended (i.e., turbidity), POM is dominated by plant matter that has not fully decomposed (i.e., detritus).

There are four major factors that affect UV light penetration in freshwater lakes: 1) chlorophyll α[10], 2) DOM, 3) suspended solids, and 4) pure water itself. Jerome and Bukata (1998) evaluated the relative absorbance of UV light in Lake Erie and Lake Waskesiu waters. They concluded that around 90% of UVA and UVB is absorbed by the combination of chlorophyll α and DOM. However, at the shortest UVB wavelengths, between 76 and 86% of UVB is absorbed by DOM while absorption by chlorophyll α is comparable to that of pure water. On the other hand, in the near visible UVA range chlorophyll α is the dominant factor. Based upon these data it appears that DOM concentration is the most important factor controlling UVB light-dependent toxicity in the aquatic environment.

Animal behavior also plays a significant role in photoxicity. Because UV light energy is capable of damaging the structure of DNA in organisms, most organisms have developed mechanisms to avoid UV light. The two most basic mechanisms are photoprotection and photoavoidance. The most obvious mechanism of photoprotection is the presence of pigmentation on the dorsal surface of all aquatic species except those that live below the level of light penetration. Persaud and Yan (2005) reported that UV tolerance and pigmentation increased with age in larvae of the midge *Chaoborus punctipennis*, and Bell et al. (2004) reported that adult midges, *Chironomus dilutus*, were much less sensitive to UV light than larvae. McNamara and Hill (1999) reported that prosobranch snails are relatively insensitive to UVB; *Elimia clavaeformis* was not affected by UVB doses that killed midges, and small *Physa gyrina* were more sensitive than larger specimens of the same genus. These results show that pigmentation and relatively thick shells convey UVB tolerance.

For many species exposure to 280-400 nm UV and shorter wavelength visible light (400-440 nm) triggers avoidance, or negative phototaxis. Negative phototaxis is a form of photoavoidance that is commonly observed in phytoplankton, zooplankton, fish and amphibians. These organisms come near the water surface only during the morning and evening when light levels are low. These UV-sensitive organisms avoid depths at which damaging wavelengths are present but seek out cover (i.e., "light niches") or depths where beneficial wavelengths for photorepair and UV vision are present. Many invertebrates also respond directly to UV light, while others merely respond to light. For instance, when natural pigmentation is not sufficient to protect from light, burrowing and cryptic behavior are the most common responses of benthic invertebrates. Not surprisingly, Bell et al. (2004) reported that midge larvae exposed to UV light in sediment were much less sensitive than when exposed in water only.

In addition, freshwater macroinvertebrates that normally inhabit or feed on the tops or sides of rocks, such as mayflies, caddisflies and blackflies, also avoid UV light. Kiffney et al. (1997) showed that such species exhibit increased drift to more shaded areas when exposed to increased UVB. Donohue and Schindler (1998) reported that blackfly larvae density was 161-168-fold lower in UV-exposed channels than in shaded channels. Hatch and Burton (1999) reported that, in the laboratory, *Hyalella azteca* avoided UV light by hiding under leaf litter when available. Other benthic organisms such as the chironomid, *Chaoborus*, can detect long wavelength UVA, but cannot detect (and avoid) short wavelength UVA or UVB (Persaud et al. 2003). Presumably, these organisms adapt by other mechanisms and avoidance is not important to these organisms in

[10] Chlorophyll a is used as a surrogate measure of phytoplankton abundance or POM.

the wild. Kelly et al. (2000) reported that benthic invertebrate population patterns are altered by both UV light and the concentrations of DOM that absorb UV light.

The ability to perceive UVB light appears to be best developed in pelagic organisms, and organisms such as daphnids and copepods appear to be able to detect and avoid UVB light (Smith and Baylor 1953; Stortz and Paul 1998; Barcelo and Calkins 1978; Leech and Williamson 2001). Fish are also negatively phototactic to UV light, and the spawning depth of perch (Williamson et al. 1997) and the nesting depth of sunfish (Gutierrez-Rodriguez and Williamson 1999), is deeper in high UV lakes compared to low UV lakes.

Not surprisingly, behavioral responses to UV-light are related to UV tolerance. Leech and Williamson (2000) reported that organisms inhabiting the surface waters of a lake in Pennsylvania were more tolerant of UV light than those inhabiting deeper waters during the day. Many fish species, such as sunfish and perch, possess UV photoreceptors as larvae but lose them with maturity and pigmentation. This loss of photoreception coincides with a habitat shift from the surface waters to deeper waters in addition to a change in diet from small to large zooplankton and/or fish (Lowe et al. 1993; Browman et al. 1993).

Photoactivation of PAHs

As discussed previously a number of recent laboratory studies have shown that the presence of UVA as well as UVB light increases the toxicity of PAHs. This increase in toxicity theoretically may occur via two different mechanisms, photosensitization or photomodification. In photosensitization, internalized PAHs directly absorb a photon that elevates the ground-state to an excited triplet state (^{3}PAH). This ^{3}PAH reacts with another PAH or water molecule to generate the PAH free radical or water free radical. These can react directly with biological ligands to cause toxicity. Photomodification reactions are similar but proceed externally and generate oxidation products from PAHs, such as quinones[11], in the aqueous medium. Both parent and product PAHs can enter the organism, and certain endogenous molecules (i.e., quenchers), such as ascorbic acid and carotenes, can deactivate the $^1O_2$ free radicals. Interestingly, although certain quinones may be theoretically more toxic than their parent molecules, DeGraeve et al. (1980) reported that hydroquinone was rapidly oxidized to *p*-benzoquinone and that the latter was degraded so rapidly to less toxic compounds that they could not estimate a chronic LC50 in fish.

Only certain PAHs can be photoactivated to release free radicals because the ability of a molecule to undergo these reactions is dependent upon its absorbance spectra. The absorbance spectra of a molecule can be expressed as the magnitude of difference between the energy required to elevate an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the so-called HOMO-LUMO gap. PAHs that undergo photosensitization are characterized by a HOMO-LUMO gap in the range of 7.24 to 7.68 eV. This group includes anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, pyrene, benzo(a)anthracene, benzo(e)pyrene, acridine, benzo(k)fluoranthene, fluoranthene, perylene, and benzo(g,h,i)perylene (Mekenyan et al. 1994). The required energy to excite PAHs to the LUMO can be produced by either UVB or UVA, depending on the specific PAH. This is important

[11] Quinones are only one of up to 30 photoproducts that have been identified.

because UVA penetrates to much greater depths than UVB and, as discussed above, it is not clear that all organisms are able to detect and avoid UVA.

Different PAHs react to UV light in different ways. Krylov et al. (1997) reported that of 16 PAHs tested, nine were more likely to be photomodified to more water-soluble products while seven were more likely to form directly reactive free radicals. For instance, anthracene, benzo(a)anthracene, and phenanthrene form quinones through photomodification, while fluoranthene produces free radicals through photosensitization. However, Barron et al. (2003) and Little et al. (2000) reported only photosensitization reactions with fish exposed to water-soluble fractions of crude and refined petroleum oils. Diamond et al. (2000) showed that under identical UVA exposure conditions, the spectral characteristics of individual PAHs could be used to predict their biological effects. Therefore, photomodification, while toxicologically interesting, may be environmentally irrelevant except that it increases the rate of PAH degradation and limits uptake by creating more water soluble compounds.

In an external medium, PAHs are degraded by UV light to more water-soluble compounds. McConkey et al. (2002) reported that naphthalene is photomodified by natural sunlight to 1-naphthol, coumarin and possibly two hydroxyquinones. They also cited mammalian studies for evidence that 1-naphthol is more toxic than naphthalene. However, Boese et al. (1998) found no difference in the toxicity of naphthalene to amphipods before and after UV irradiation. This may be due to the relatively low yield of 1-naphthol created under bioassays conditions versus the high yield created by McConkey el al. (2002) in their efforts to create photoproducts in detectable amounts. Certainly, under field conditions where the parent compound is present in toxic concentrations, photomodification products would be present in lower concentrations. Another possible explanation is that 1-naphthol is not taken up as efficiently as naphthalene. Regardless, there is no evidence that naphthalene or alkylnaphthalenes, undergo photosensitization reactions.

Nevertheless, photomodified PAHs may play an important role in the degradation of other PAHs. For instance, 1-naphthol is a photoactivator for other aromatic compounds that do not absorb UV light, such as alkylbenzenes (Payne and Phillips 1985). Multiple photooxidation products of alkylbenzenes have been detected in surface waters (Ehrhardt and Burns 1990). UV light not only affects the concentrations of PAHs, but their composition as well. Ehrhardt et al. (1992) reported that alkyl-substituted benzenes and PAHs and heterocyclic PAHs are preferentially degraded to ketones and aldehydes in surface waters. Aldehydes are effective cross-linking agents that could cause adverse effects on aquatic organisms, but they are also less lipophilic and less likely to be accumulated by the organism. It is not known if these compounds are more or less toxic to aquatic organisms, but DOM is also photo-degraded to aldehydes and ketones (Mopper and Stanhovec 1986) and microbes in the water column readily consume these photoproducts. The same degradation and metabolism would be expected of photomodified PAHs.

Because photosensitized PAHs are only effective when released inside the body, only bioaccessible PAHs can cause toxicity through this mechanism. The bioavailability[12] of PAHs is governed by their aqueous and lipid solubility, and these in turn are governed by the compound-

[12] Bioavailability refers to a bioaccessible compound that can be taken up across biological membranes. Not all bioaccessible compounds are bioavailable.

specific octanol-water partition coefficient (Kow). However, not all of the routinely measured PAH body burden is internal and bioavailable to cause phototoxicity. Bell et al. (2004) reported that the exuviae (the exoskeleton shed by the pupa when molting to the adult stage) of chironomids contained higher concentrations of fluoranthene than the whole body tissue, and that emerging adults contained seven-times less fluoranthene than 4th instar larvae.

The ability to create photosensitivity using UV light under laboratory conditions does not necessarily mean that toxicity will occur under natural conditions. Since PAHs must be exposed to UV light in order to be photoactivated, it is not surprising that, although photomodified PAHs have been reported in surface waters, they have not been found in sediments (Ehrhardt and Burns 1993) where they are not exposed to UV light. Similarly, although PAHs are photosensitized and cause toxicity when exposed in the water column, thin layers of sediment protect benthic invertebrates from photosensitization (Ahrens and Hickey 2005). Boese et al. (1998) also reported that the compounds with the lowest water solubilities (i.e. HMW PAHs) were the least phototoxic in sediment bioassays because these compounds were bound to organic matter and not available for uptake. Therefore, the ability to create photosensitity under laboratory conditions does not necessarily mean that toxicity will occur under natural conditions.

In addition, UV light also increases the sensitivity of organisms to stressors other than PAHs. For instance, UV light increases the toxicity of arsenic to *Ceriodaphina dubia* (Hansen et al. 2002), probably as a simple additive stress or through inhibition by arsenic of intrinsic DNA and/or protein repair mechanisms. Retene, a natural product found in wood chips and common near pulp mills, is also photosensitized and causes enhanced toxicity (Hakkinen et al. 2003). In field samples it may be difficult to separate the effects of UV light and PAHs from those of the multiple environmental contaminants inevitably present.

Relevance of Phototoxicity of PAHs to the Natural Environment

The effect of UV light on PAH-induced toxicity is an area of current academic research that is poorly understood and may not be relevant to the natural environment. McDonald and Chapman (2002) have discussed a number of factors in the photo-toxicity literature that call into question the relevance of the UV studies that have been conducted. For instance, laboratory bioassays do not mimic natural conditions because different wavelengths have different intensities during the day as the angle of the sun to the water surface changes and spectral changes alter phototoxicity. These conditions are not faithfully duplicated in the laboratory. Laboratory studies also do not include the dissolved organic matter and suspended solids that reduce PAH bioaccessibility. McDonald and Chapman (2002) summarized that "To date there have been no studies that clearly and directly implicate PAH phototoxicity with adverse ecological effects in field populations" and referring to the association between UV light and toxicity in the laboratory, "This likelihood has been unrealistically increased in all published studies of PAH phototoxicity".

This perspective is supported by remarks by Swartz et al. (1997) who concluded that photo-activation of PAHs "may be toxicologically correct but ecologically irrelevant because infaunal burrowing amphipods...are rarely, if ever, exposed to UV radiation". Likewise, as mentioned previously, Hatch and Burton (1999) found that *Hyalella azteca* avoided UV light by hiding under leaf matter when provided the opportunity, and Diamond et al. (cited in McDonald and

Chapman 2002 as in preparation) noted that "in nature these organisms are protected by extensive water column attenuation, shading, and are strongly thigmotactic".

Were the effects levels of PAHs and UV light found in the laboratory indicative of those found in the field, McDonald and Chapman (2002) concluded that "large areas of shallow aquatic environments should be depauperate, yet this is not the case." This would be particularly true of commercial waterways, urban estuaries, marinas, and receiving water of surface runoff. Yet this is not true.

For the reasons discussed in this section, endpoints based upon bioassays under UV light will only be considered as an uncertainty in this BERA.

5.1.2.2 Effects of PAHs to Benthic Invertebrates

As discussed in Section 3.11.1, four lines of evidence were used to evaluate the potential effects of Site related PAHs in sediment. These included:

1) Comparison of bulk sediment chemistry concentrations to WDNR sediment quality guidelines;
2) Levels of PAHs and VOCs in *Lumbriculus variegatus* tissue compared to a no observed effect body residue (NEBR) developed using the target lipid model (TLM) [DiToro et al. (2000)];
3) Sediment bioassays; and
4) A benthic macroinvertebrate community investigation.

Bulk Sediment Chemistry

The maximum concentrations of chemicals in sediment were first compared to the WDNR sediment quality guidelines (WDNR 2003) or, where these guidelines were not available, other benchmarks listed in Table 3-4. Contaminants that exceeded these values were then further evaluated as described below.

Tissue Residues of PAHs and VOCs in Benthic Invertebrates

As previously discussed, numerous studies have shown that PAHs exert toxicity on aquatic organisms via narcosis. Narcotics act by occupying a certain set volume within neural membranes. As a result, a number of small narcotic molecules that occupy the same molar volume as one large narcotic molecule causes the same degree of narcosis. This means that the toxicity of multiple narcotic chemicals can be estimated by the sum of their molar volumes. This is called the critical body residue (CBR). Numerous studies have also shown that the CBR in body lipids provides a better estimate of the toxic concentrations than either sediment or water benchmarks. This is because the concentration in body lipids accounts for both bioaccessibility and bioavailability.

The Target Lipid Model of DiToro et al. (2000) was used to evaluate the toxicity of PAHs and VOCs in benthic invertebrates as well as fish. The TLM combines the CBR concept with equilibrium partitioning (EqP) to calculate the no effect body residue (NEBR). The TLM method is described below.

DiToro and McGrath (2000) compiled the available acute toxicity data (i.e., aqueous LC50s) for 33 species of aquatic organisms exposed to 156 narcotic chemicals. The authors then used EqP to calculate the residue of each chemical in the animal body lipid. EqP results from the propensity of nonpolar organic chemicals to avoid water and seek other organic compounds, such as body lipids. Then, using the same method used by U.S. EPA to develop water quality criteria, they rank ordered the LC50 data and selected the lowest 5th percentile tissue residue (the residue that causes no effects on 95% of all species tested) as the CBR. This CBR, 35.3 μmol/g lipid, is the body residue that will cause 50% lethality in an estimated 5% of aquatic organisms. In order to estimate the chronic no effect body residue (NEBR), they divided the CBR by an acute-to-chronic ratio (ACR, 5.09) that was derived from acute and chronic toxicity data for 20 chemicals and six species. This means that the no effect concentration is approximately 5-fold lower than the LC_{50} concentration. Dividing the CBR by 5.09 results in a NEBR of 6.94 μmol/g lipid.

However, DiToro et al. (2000) realized that different categories of organic chemicals cause narcosis at different CBRs. Therefore, they divided the available toxicity into six different categories, one of which was PAHs. Compared to the overall (baseline) NEBR of 6.94 μmol/g lipid, PAHs are approximately twice as toxic. Therefore, the NEBR for PAHs was modified by a factor of 0.546. The resulting NEBR for PAHs is 3.79 μmol/g lipid. The NEBR for VOCs is no different from the baseline NEBR, 6.94 μmol/g lipid (McGrath et al. 2005).

As discussed greater detail below and in Appendix B, 28-d sediment bioaccumulation tests were conducted with the aquatic oligochaete worm, *Lumbriculus variegatus*. The results of this bioassay were used as the basis for modeling the uptake of contaminants from Site sediment by Site benthic macroinvertebrates. The predicted tissue concentrations in Site macroinvertebrates were then compared to the NEBR for PAHs. Section 5.1.2.3 will discuss how this benchmark was also compared to the actual tissue concentrations in wild fish collected at the Site.

Site-specific Sediment Bioassays

The third line of evidence for evaluating the potential toxicity of sediments was through conduct of site-specific bioassays. Bioassays were conducted with the sensitive benthic invertebrates *Hyalella azteca* (amphipod) and *Chironomus dilutus* (midge). The results of these bioassays are presented in more detail in Appendix B (Attachment 2: Sediment Bioassays).

Exposure of laboratory organisms to Site sediments in the laboratory was used to determine the levels of sediment contaminants that were associated with adverse effects to laboratory animals. Because these sediments contain all of the Site COPCs, the results of these tests represent the cumulative toxicity of all of the COPCs, not just the PAHs. However, of the COPCs measured in sediments PAHs were, by far, the most widespread and had the highest level of any COPC. Therefore the focus of this discussion will be on the potential effects of PAH.

The following summarizes the results of toxicity tests using Site sediment that were conducted in 2005-2006. Details of these tests are provided in Appendix B: Attachment 2.

Hyalella azteca

There was significant mortality to *H. azteca*, generally the most sensitive organism used in sediment bioassays, in all of the Reference Sand sediments collected in 2005-2006. Furthermore the mortality was consistent in four different Reference Sand stations collected from four different locations in Chequamegon Bay and at two different times four months apart. In addition, this mortality was observed during three different bioassays with *H. azteca* during three different bioassays conducted months apart. This strongly suggests that there were unmeasured variables that affected the outcome of the bioassays and that not all of these adverse effects were attributable to Site-related contaminants (Appendix B: Attachment 2).

When compared to silica sand control treatments in 2005-2006, only Site sediment SQT1 and SQT7 showed significant and consistent mortality under normal laboratory light conditions. Based upon the results of the *H. azteca* bioassays a no effect concentration (NOEC) of 4536 µg PAH/gOC (20.9 µg PAH/g; 0.46%OC) and a low effects concentration (LOEC) of 6084 µg PAH/gOC (22.5 µg PAH/g; 0.37 %OC) was indicated (Table 5-1).

SEH (2001) reported a slightly higher NOEC for *H. azteca,* 9,978 µg PAH/gOC (249.4 µg/g; 2.5%OC), and a LOEC of 14,396 µg PAH/gOC[13] (823.1 µg/g; 5.7%OC) (Table 5-2).

Table 5-1. Results for Sediment Bioassays 2005-2006.

Summary of Normal Light Bioassay Results with Three Species for URS 2005-2006				
Organism	NOEC		LOEC	
	Total PAHs µg/g	Total PAHs µg/gOC	Total PAHs µg/g	Total PAHs µg/gOC
H. azteca	20.9	4,536	22.5	6,084
P. promelas	22.5	6,084	166.9	36,291
C. dilutus	NA	NA	NA	NA

Table 5-2. Results for Sediment Bioassays 2001.

Summary of Normal Light Bioassay Results with Three Species Conducted for SEH 2001				
Organism	NOEC[1]		LOEC[1]	
	Total PAHs µg/g	Total PAHs µg/gOC	Total PAHs µg/g	Total PAHs µg/gOC
H. azteca	249.4	9,978	823.1	4842 or 14396[2]
P. promelas	79.9	3,996	249.4	9978
C. tentans	16.2	735	79.9	3996

1) SEH reports that the NOEC and LOEC are for lowest of either mortality or growth endpoints (reduced growth or mortality > 20%

2) The first value is suspect due to apparent problems with TOC analyses. The second vaue assumes that the true TOC lies between adjacent higher and lower values.

Chironomus dilutus

Low survival with *C. dilutus* at all 6 reference stations during the 2005-2006 bioassays made evaluation of Site sediment inconclusive. The failure of chironomid larvae bioassay to settle

[13] This value has been corrected from the original report. See discussion in Appendix B: Attachment 2.

could have been due to sediment avoidance related to either chemical or physical reasons (Appendix B: Attachment 2).

SEH (2002) reported a NOEC of 735 µg PAH/gOC (16.2 µg PAH/g; 2.2%OC) for *C. dilutus* in sandy sediments (Table 5-2). The LOEC of 3,996 µg PAH/gOC (79.9 µg PAH/g; 2.0%OC) resulted in only 10% survival difference from the control (71.5 vs. 82.5%), or 90% of the control value.

Bioassays were also conducted with the fathead minnow, *Pimephales promelas.* The results of these tests are treated below in Section 5.1.2.3 (Effects of PAHs on Fish).

Proposed NOECs and LOECs based upon all bioassay studies are summarized in Table 5-3. See Appendix B: Attachment 2 for a discussion.

Table 5-3. Proposed NOECs and LOECs Based Upon Bioassay Results for 2001 and 2005-2006.

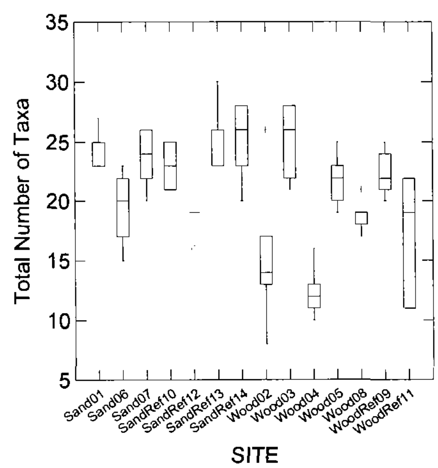
Proposed NOECs and LOECs Considering both the 2001 and 2005-6 Bioassays.		
	NOEC	LOEC
Organism	Total PAHs ug/gOC	Total PAHs ug/gOC
H, azteca	4536	6084
P. promelas	5040	23135
C. tentans	735	3996
3 Species Average=	3437	11072

<u>*Site-specific Benthic Macroinvertebrate Studies*</u>

Lastly, a benthic community investigation was conducted to evaluate whether the presence of contaminants in Site sediment resulted in any changes to benthic community structure relative to reference stations. The results of this investigation are presented in more detail in Appendix B: Attachment 3.

Taxa richness was variable amongst stations with number of taxa at each station ranging from 8 to 30 (average = 20.9). The total number of unique taxa for all stations was 133. With the exception of two stations, Site Wood SQT2[14] and Site Wood SQT4, there was no substantial difference in the average number of taxa across all station replicates (Figure 5-1).

Figure 5-1.Number of Taxa at Triad Stations.



The dominant taxa were chironomids which made up an average 32.6% (maximum 84 to 91% in the five replicate samples from Sand Reference SQT12) of the abundance in each sample. In all, 58 taxa of chironomids were identified (Figure 1 in Appendix B: Attachment 3). The next most abundant taxa were a sabellid polychaete (*Manayunkia speciosa),* oligochaetes (primarily tubificids), nematodes, an isopod (*Caecidotea racovitzai),* amphipods (including *Gammarus*

[14] SQT is a station designator meaning sediment quality triad.

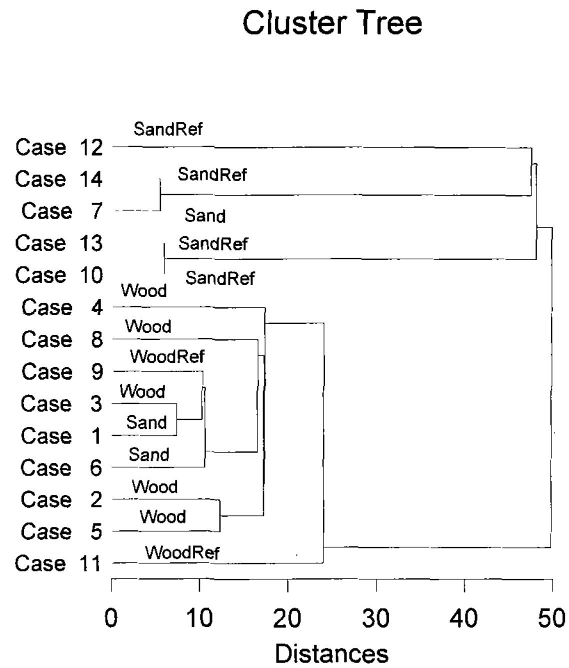
fasciatus), the unionid snail (*Amnicola limnosa*), sphaerid clams (including *Pisidium* spp.), mayflies, and caddisflies. Together these ten taxa made up approximately 94% of the total number of individuals. Chironomids and tubificids alone made up approximately 50% total number of individuals. Aquatic insects made up 75% of the taxa; the majority of these were chironomid taxa.

Very few patterns in the distribution of the taxa were discerned and only two appeared to be possibly related to the levels of PAHs (either total PAHs (TPAH) or total carbon normalized PAHs (NOC-PAH) (Figure 2 in Appendix B: Attachment 3). The epibenthic isopod, *C. racovitzai,* was more abundant at Site Wood stations, than at Reference Wood, Reference Sand or Site Sand Stations. The unionid snail, *A. limnosa,* also an epibenthic species, was absent from all of the Site Wood Stations but was present at Reference Sand, Site Sand and Reference Wood stations. Its exclusion from the Site Wood stations may be due to a combination of PAH levels and/or wood mulch substrate. Other than that example there did not seem to be a consistent pattern in the distribution of dominant taxa. *M. speciosa* was abundant at Reference Sand Stations SQT 13 and SQT14, but it was even more abundant at Site Sand Station SQT 7, a station where NOC-PAH ranged from 1014 to 62,900 µg/gOC. Likewise tubificids were abundant at Reference Sand Stations SQT10, SQT13 and SQT 14 but were also abundant at Site Sand Station SQT7. Mayflies (Ephemeroptera) were abundant at Reference Sand Stations SQT13 and SQT14, but were also abundant at several Site Sand stations (Appendix B: Attachment 3).

Review of the box and whisker plots indicated that there was substantial variation amongst replicate samples for most variables, including PAH levels, organism density and all benthic community metrics, at most of the stations. Examination of these plots did not indicate any obvious relationships with the levels of PAH (either as TPAH or NOC-PAH) (Appendix B: Attachment 3).

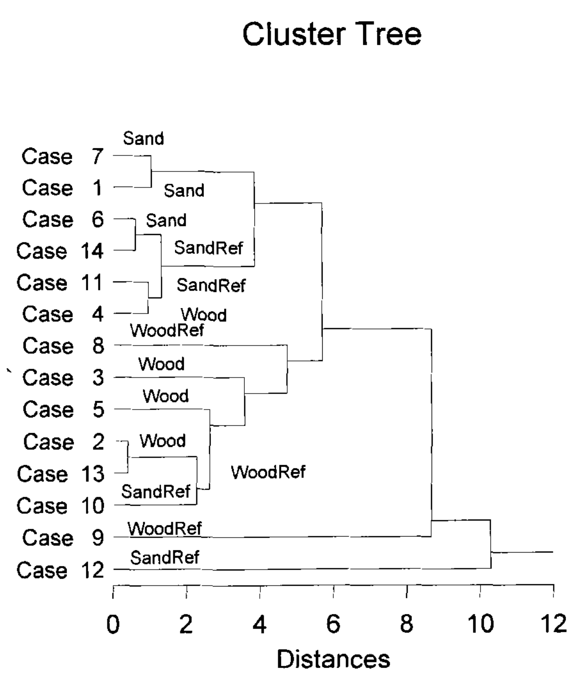
Results of the cluster analysis indicated few stations of the same substrate category were similar (Figure 5-2). Site Sand Station SQT1 was very similar to Site Sand Station SQT7 when the proportion of tolerant, facultative and intolerant taxa was considered (Figure 5-3). These two stations are both sand substrate, are adjacent to one another, and have the highest levels of NOC-PAHs. However, when clusters were based upon other metrics such as functional grouping (Figure 5-1) SQT7 was very similar to some of the Reference Sand stations such as SQT14 and quite different from SQT1. Three of the Site Wood Stations (SQT4, SQT8 and SQT2) were similar based upon percent functional groups. Based upon other metrics, however, Site Wood stations were very similar to Reference Wood stations.

Figure 5-2. Cluster Diagram Based Upon All Biological Metrics.



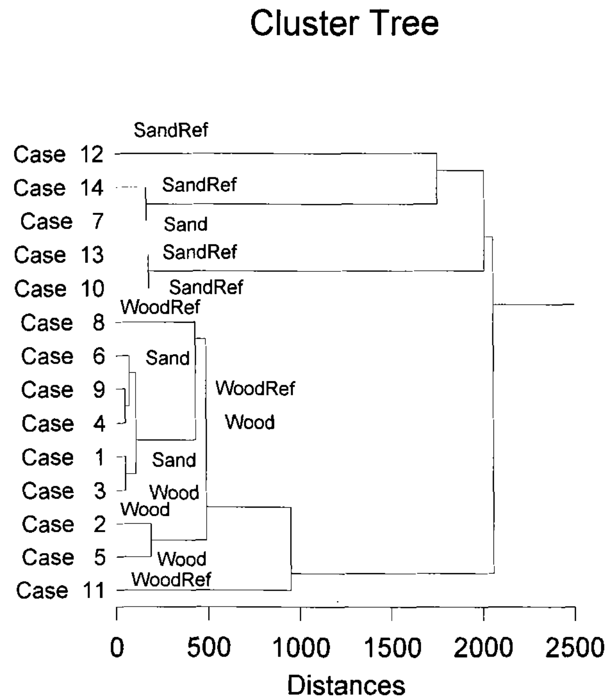
"Case" Number on Cluster Trees is the same as SQT Station Number.

Figure 5-3. Cluster Diagram Based Upon Percent Relative Tolerance.



"Case" Number on Cluster Trees is the same as SQT Station Number.

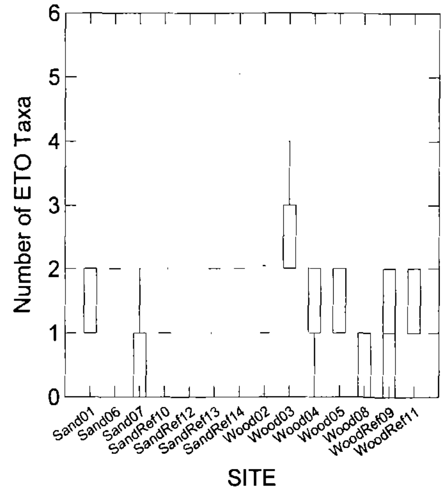
Figure 5-4. Cluster Diagram Based Upon Percent Functional Groups.



"Case" Number on Cluster Trees is the same as SQT Station Number.

Statistical analyses were conducted to evaluate whether contaminants in the sediment explained any of the differences observed in the benthic community structure. The results of the analysis of covariance (ANCOVA) indicated few significant relationships between the benthic community metrics and the level of PAHs, either as TPAH or NOC-PAH. In fact, with the exception of two metrics, the number of Ephemeroptera, Trichoptera, Odonata (ETO) taxa and the ratio of ETO/ ETO + chironomid abundance, all significant relationships indicated that as TPAH or NOC-PAH increased, the biological metric increased. These results suggest that the putatively most sensitive taxa, Ephemeroptera, Trichoptera, Odonata are negatively affected by increasing levels of NOC-PAHs. The negative relationship of the ratio of ETO/ETO+chironomid abundance to NOC-PAH levels suggest that the number of chironomids are positively related to NOC-PAHs, i.e., the chironomid abundance increased as NOC-PAH levels increased. However the paucity of ETO taxa at each station (0 to 4 taxa) indicates that not much weight should be placed upon the negative relationship between ETO taxa and levels of NOC-PAHs (Figure 5-5).

Figure 5-5. Number of ETO Taxa at Triad Stations.



The nature of the substrate and grain size had a much greater influence on benthic community metrics than did the level of PAHs. Based upon the step-wise regression and the one-way ANOVA, grain size and substrate type were significant explanatory factors for the variation in the benthic community. For most of the benthic community variables the finer grain sizes were associated with lower values.

The overall results suggest that PAH levels (whether TPAH or NOC-PAH) are playing only a minor role in structuring communities, overshadowed by other substrate effects (e.g., grain size and whether the substrate category was wood or sand). Perhaps this is not surprising as it was expected that a benthic community inhabiting an area with a wood mulch substrate would differ from that inhabiting a sand substrate. It has also been well-established in benthic ecology that grain size and substrate type is often a significant explanatory factor of differences in benthic community structure.

Summary of Lines of Evidence for Benthic Invertebrates – Sediment Quality Triad

In summary, bulk sediment chemistry suggests that compared to WDNR sediment quality guideline (WDNR 2003) there should be a no effects threshold between 1.6 and 22.8 μg/g in sediment with 1% organic carbon (@1%OC). The results of the sediment bioassays conducted in 2001 and 2005-2006 indicate that the no effects threshold for benthic invertebrates such as *H. azteca* in the range of 4500 to 10,000 μg PAH/gOC. These levels are equivalent to 45 to 100 μg/g @1%OC. For benthic invertebrates like *C. dilutus* a no effects level is predicted at about 735 μg PAH/gOC (or 7.35 μg/g @1%OC).

No significant effects appear to be manifested at the benthic community level of organization even in areas where PAH levels from benthic samples were in the range of 40,000 to 80,000 μg PAH/gOC (400 to 800 μg/g@1%OC) at individual Triad stations samples (Appendix B: Attachment 1). However, there was tremendous variability and resultant uncertainty associated with both the site samples and reference samples collected in the benthic macroinvertebrate community investigation.

5.1.2.3 Effects of PAHs on Fish

Surface water Chemistry

The potential toxicity of surface waters at the Site was evaluated in three different manners. Maximum concentrations of chemicals were first compared to the Region V ESLs (USEPA 2003a) or equivalent criteria as discussed in Section 3-5 (Table 3-3). No chemicals exceeded these values.

Two further lines of evidence are also presented. The first entailed the collection and analysis of wild fish from the Site and the second relied on bioassays conducted with early life stage *Pimephales promelas* (fathead minnow). The fish tissue PAH, VOC and lipid data were treated as described above for *L. variegatus*, using the NEBR. The results of these bioassays are presented in Appendix B and summarized here.

Tissue Residues of PAHs in Wild Fish

The bioaccumulation of PAHs in three species of wild fish was measured for two purposes. First, as discussed above, using the TLM of DiToro et al. (2000) the body residues of PAHs were used to evaluate risk to the fish community. Secondly, the body residues were used in the food chain model to calculate the doses to wildlife that ingest fish (Section 5.2).

Whole small-mouth bass, brown bullhead and smelt were caught from the Site and the concentrations of PAHs in the whole body were measured. Using the same methodology as described for the worm bioassay, the lipid-normalized concentrations of VOCs was also estimated. The resulting PAHs were compared to the baseline NEBR of 3.79 μmol/g lipid for PAHs (DiToro et al. 2000). None of the fish collected contained a concentration of PAHs or VOCs greater than the NEBR.

Site-Specific Sediment Bioassay

As expected for a receptor that does not normally contact the sediment, fathead minnow larvae were relatively insensitive to PAHs in bulk sediments, with no mortality reported at 36,291 μg PAH/gOC (166. 9 μg PAH/g; 0.46%OC) in 2005-2006 (Table 5-1). There was a significant growth effect at that concentration however and that value was considered as a LOEC. The NOEC for this bioassay is 6,084 μg PAH/gOC (22.5 μg PAH/g; 0.37%OC). However, the NOEC in 2001 was 3,996 μg PAH/gOC (79.9 μg PAH/g; 2.0%OC) in 2001 (Table 5-2). The average of these two NOECs (5,040 μg PAH/gOC) is proposed as the NOEC and the average of the two LOECs, 23,135 μg PAH/gOC (22.5 μg PAH/g; 3.6%OC) is proposed as the LOEC (Appendix B: Attachment 2 and (Table 5-3).

5.1.3 Effects of PAHs on Wildlife

As discussed above, tars are composed of four major categories of compounds, aromatics, saturates (alkanes, paraffins), resins, and asphaltenes. However, as with aquatic organisms, not all of these components are toxic to terrestrial organisms. Because toxicological studies have been conducted with small mammals as surrogates for humans, there is much more toxicological data for mammals than for birds. In mammals, LMW and HMW PAHs and short-chain alkanes may cause toxicity, but neither resins nor asphaltenes are toxic. A few studies have also shown that these compounds are non-toxic to birds. In wild mammals, both LMW and HMW PAHs can cause toxicity, but because they are volatile, the VOCs such as benzene and the alkylbenzenes, are unlikely to get into the food chain unless there is an ongoing source. As a result, most laboratory toxicity data for VOCs has focused on inhalation in confined spaces, but oral ingestion studies have been conducted on mammals with BTEX compounds. No literature concerning the toxicity of VOCs to birds was identified. However, only burrowing species could reasonably be expected to be exposed to potentially toxic concentrations if there were VOCs in soil. However VOCS were not identified as COPCs for soil; therefore, with regard to ecological exposure pathways, most studies have focused on the PAHs. Therefore, with regard to ecological exposure pathways, most studies have focused on the PAHs. Furthermore, in this BERA,

The two major exposure pathways for wildlife are the diet and soil or sediment that is incidentally ingested during feeding, grooming, or preening. The composition of the PAHs in these pathways is very different. Both HMW and LMW PAHs may be acquired through incidental soil ingestion, but PAHs do not accumulate in small mammals or birds (US EPA. 2005) and Site-specific fish tissue data reveal only LMW PAHs. Therefore, TRVs for HMW and LMW PAHs are relevant for incidental soil or sediment ingestion while only TRVs for LMW PAHs are relevant for the diet.

5.1.3.1 Birds

The PAHs that have been detected in fish samples from the Site reflects the composition expected from the more water-soluble fraction of site sediments. Nearly all PAHs detected in fish tissues from the Site were LMW PAHs. (Appendix C). Therefore, it is assumed that LMW PAHs are the dominant form that would be ingested by piscivorous bird species. On the other hand, worms from the bioaccumulation study, which will be used as surrogates for invertivorous wildlife, contained HMW, as well as LMW PAHs. The avian toxicity studies evaluated for both LMW and HMW PAHs are discussed below.

Toxicity studies that reflect the composition of PAHs found in fish tissues were selected for evaluation to derive representative TRVs. Only one chronic study evaluated the toxicity of LMW PAHs on birds. The following describes the bioassays and their results.

The best quantitative chronic study is that conducted by Patton and Dieter (1980). These authors fed mallard ducks an artificial mixture of 400 or 4000 mg PAHs/kg diet for 7 months, and reported no mortality or symptoms of toxicity in any of these tests when compared to control animals. Patton and Dieter (1980) reported the relative composition of the PAH mixture used in the study, but not the individual concentrations of percentages. However, the authors stated that the compounds were present at concentrations that were equimolar to that found in South Louisiana crude oil. The mixture also contained ethylbenzene, two sulfur heterocycles, and 2,6-dimethylquinone. Since only one of the ten aromatics was a monoaromatic (VOC), it was assumed that the mixture was representative of a LMW PAH mixture.

Patton and Dieter (1980) reported no growth or survival responses related to the LMW mixture; however, an adaptive physiological response to mallards ingesting 4000 mg PAHs in their diet was observed. Ingestion of 4000 mg PAHs caused an increase in liver weight, hepatic blood flow, and indocyanine green clearance rate (a marker of liver function). No plasma enzyme markers of organ injury were elevated above control values. The increase in liver size, blood flow and dye clearance rate indicated that the ducks had adapted to the contaminated diet. Exposure to 400 mg PAHs/kg diet resulted in little physiological and no biochemical response.

Given that no effects on growth or survival were observed, the dose calculated from the dietary concentration of 4000 mg PAH / kg is considered a NOAEL dose. The designation of this dose as a NOAEL is consistent with USEPA guidance, which does not consider a physiological response an adverse effect in its derivation of ECO-SSL values. However, at the direction of USEPA in its comments on the draft BERA, an additional conservative NOAEL is calculated based on the dietary concentration of 400 mg PAH / kg.

The ducks in Patton and Dieter (1980) weighed about 1300 g. Using the allometric dry weight food ingestion rate for galliformes (Nagy 2001) results in a food ingestion rate of 0.04 kg/kg BW/day. Diets containing 400 or 4000 mg PAHs/kg result in the following NOAEL doses:

$$NOAEL = 4000\ mgPAH/kg\ x\ 0.04\ kg/kg\ BW/day$$
$$= 161\ mg\ PAH/kg\ BW/day$$

$$NOAEL = 400\ mgPAH/kg\ x\ 0.04\ kg/kg\ BW/day$$
$$= 16.1\ mg\ PAH/kg\ BW/day$$

Because worms from the bioaccumulation study conducted to support this BERA contained HMW PAHs, a chronic study that evaluated the potential toxicity of these compounds was also evaluated. Only one study was found. Stubblefield et al. (1995) fed 5-day old mallard ducklings 0, 200, 2,000, or 20,000 mg/kg BW/day weathered Prudhoe Bay crude oil (WPBCO) for 20-weeks and reported no adverse effects on reproduction; ducklings did not avoid WPBCO. While Stubblefield et al. (1995) did find reduced eggshell thickness and changes in plasma electrolytes, they also reported that there were no adverse effects on the ability of parental birds to produce viable embryos, the rate of hatch success, or the survival and fitness of the resulting chicks. Therefore, eggshell thinning is considered a physiological and not a reproductive effect. Consistent with USEPA guidance for deriving ECO-SSLs, physiological responses are not considered adverse effects in calculating TRVs.

Stubblefield et al. (1995) reported a final body weight of 1250 g and a food ingestion rate of 132.5 g/bird/day. Based upon a dietary concentration of 20,000 mg/kg BW/day, the NOAEL for HMW PAHs is:

$$NOAEL = \frac{20{,}000\ mg/kg\ food\ x\ 0.1325\ kg/day}{1.25\ kg\ BW}$$
$$= 2120\ mg\ HMW\ PAH/kg\ BW/day$$

Since the diet usually comprises the majority of the total exposure in wildlife, the lower of these TRVs, those from the Patton study, 16.1 and 161 mg PAH/kg BW/day, will be used in this

BERA as the avian TRVs for PAHs (Table 5-4). This is conservative because the sum of all PAHs will be compared to the lower TRV for LMW PAHs.

5.1.3.2 Mammals

Fish-eating mammals, such as the mink, may also be exposed to PAHs in their diet at the Site. Since the PAHs in the fish collected from the Site were largely LMW PAHs, and the largest component of the LMW PAHs at the Site is naphthalene, this compound was selected to represent all LMW PAHs. Two studies of naphthalene were evaluated, one a chronic study, and the other an early life stage study. Shopp et al. (1984) fed mice 5.3, 53, or 133 mg naphthalene/kg BW/day for 90-days and reported no adverse effect on body weight or survival. Female, but not male, mice exhibited increased spleen weight at the highest dose. The authors concluded that naphthalene doses up to ¼ the LD50 caused no biologically-relevant effects. Therefore, the NOAEL from this study was 133 mg LMW PAH/kg BW/day.

Plasterer et al. (1985) administered naphthalene to CD-1 mice for eight days starting on the seventh day of gestation and reported an LD50 of 354 mg/kg BW and an LC0 of 250 mg/kg BW/day. The 250 mg naphthalene caused a significant decrease in dam body weight and 300 mg/kg BW/day caused a 15% decrease in maternal survival. The latter dose caused no significant decrease in the reproductive index, but reduced the average number of pups. Since there was not a concomitant decrease in dead pups, this was likely due to an increased number of embryonic resorptions. The pups that were delivered were normal and healthy. No adverse effects on either generation were found at 125 mg naphthalene/kg BW/day.

The geometric mean of these two early life-stage no effect doses (133 and 125 mg naphthalene/kg BW/day) was selected as the NOAEL for mammals exposed to LMW PAHs through the diet (Table 5-5).

$$TRV_{NOAEL} = 129\ mg\ LMW\ PAH / kg\ BW / day$$

Based upon the bioaccumulation tests with *L. variegatus*, were mink to ingest benthic invertebrates, they might also be exposed to HMW PAHs. Therefore, three studies with HMW PAHs were evaluated. Springer et al. (1989) reported that administration of 740 mg tar/kg BW/day to rats during days 12 to 14 of gestation had no adverse effects on the number of live births, but was associated with a significant increase in early mortality in pups and in dams. Therefore, this study was not considered further for the NOAEL.

Culp et al. (1998) fed female B6C3F1 mice 0, 0.01, 0.03, 0.1, 0.3, 0.6, and 1% tar for 2-years and reported a decrease in body weight at doses of 1,364 and 2,000 mg/kg BW/day, but not at 628 mg tar/kg BW/day. However, in a simultaneous study with a different tar containing elevated levels of BaP, they reported a 20% weight loss at doses of 333 to 346 mg tar/kg BW/day. The differences in these effects on body weight is likely due to differences in the component mixtures of these different fresh tars and the age of initial exposure. The authors attributed their weight losses to food avoidance, rather than toxicity. Laboratory mice normally live less than 2-years and older wild mice live less than 1 year (U.S. EPA 1993) or are culled by predation. Therefore, this study was not considered further for the NOAEL.

Weyand et al. (1995) administered 0.05, 0.25, or 0.5% MGP residue, a type of tar formed as a by-product of coal gasification, to B6C3F1 mice for 185-days and reported no adverse effects on survival, growth, development, hematology, histopathology, clinical chemistry, or reproduction at a dose of 462 mg/kg BW/day.

Since the objective of ecological risk assessments is protection of animal populations and mice are reproductively mature at 6- to 8-weeks, the 185-d no effect doses of Weyand et al. (1995) were selected as a conservative NOAEL for small mammals ingesting HMW PAHs (Table 5-5). Therefore:

$$TRV_{NOAEL} = 462\ mg\ HMW\ PAH\ /\ kg\ BW\ /\ day$$

For the purposes of this BERA, only the lower TRV for LMW PAHs was used for mammals (Table 5-5). This is conservative because the sum of all PAHs will be compared to the lower TRV for LMW PAHs.

5.1.4 Effects From Other Contaminants of Concern

In addition to PAHs, VOCs and several metals were higher than the screening values for sediment and soil quality. VOCs included dibenzofuran, m, o and p-cresol, and the BTEX compounds in sediment. Metals included barium, copper, selenium and thallium in sediment and antimony, cadmium, lead, manganese, mercury, selenium and zinc in soil. In addition, one PAH, dibenzofuran, exceeded screening levels.

5.1.4.1 Benthic Invertebrates

No benchmarks were derived for metals in sediment. However, the results of SEM:AVS analysis were used to evaluate the bioavailability of any divalent metals in the sediment. Since metals make up such a minor portion of COPCs in the sediment WDNR Sediment Quality Guidelines (WDNR 2003) were used for risk estimates from these metals. As discussed in Section 5.1.2.2, VOCs were evaluated along with PAHs by comparing the NEBR to estimated body burdens in the bioassay worms.

5.1.4.2 Fish

As discussed in Section 5.1.2.3 VOCs were evaluated along with PAHs by comparing the NEBR to estimated body burdens in wild fish collected at the Site. Metals in surface water or fish tissue were not measured. Not only do metals make up such a minor portion of COPCs in the sediment, but use of BSAFs to estimate fish metals levels is an unreliable way to evaluate the potential for adverse effects. This is because different species of fish have different mineral requirements and contain different levels of metals, naturally, and because the sediment-to-fish exposure pathway is poorly understood. Most studies have shown that the major exposure pathway for fish to metals is through the dissolved ions present in the water column. Some other studies have shown that metals can be accumulated through the diet, but these studies have identified risks from this pathway only at mine sites where metals are the major contaminants and both invertebrate and sediment levels are far higher than at the Site. Since there were no exceedances of screening benchmarks for metals in surface water, there is little reason to believe that metals would be elevated significantly above normal levels in Site fish.

5.1.4.3 Birds

The following TRVs were derived for metals and summarized in Table 5-4. No TRVs for VOCs were derived because no adequate studies were identified. Avian exposure to VOCs is considered an uncertainty in the assessment.

Antimony

No avian ECO-SSLs have been proposed because there is no toxicity data for birds exposed to antimony. Therefore, no TRVs are proposed for antimony for birds for this risk assessment.

Barium

No avian ECO-SSL has been proposed. Based on work by Johnson et al. (1960), Sample et al. (1996) calculated a NOAEL of 208.3 and a LOAEL of 416.5 mg Ba/kg BW/day.

NOAEL = 208.3 mg Ba/kg BW/day

LOAEL = 416.5 mg Ba/kg BW/day

Cadmium

At the direction of USEPA, avian TRVs for cadmium were based on reproduction and growth endpoints from studies used to derive the ECO-SSLs (USEPA 2005a). The NOAEL (1.47 mg Cd/kg BW/day) was based on the geometric mean of NOAELs for growth and reproduction from these studies. The LOAEL (6.3 mg Cd/kg BW/day) was based on the geometric mean of LOAELs for growth and reproduction (USEPA 2005a).

NOAEL = 1.47 mg Cd/kg BW/day

LOAEL = 6.3 mg Cd/kg BW/day

Copper

The avian NOAEL for copper was based on the geometric mean of NOAEL endpoints from growth and reproduction studies used to derive the ECO-SSL for copper (18.4 mg Cu/kg BW/day; USEPA 2005a). The LOAEL was based on the geometric mean of LOAEL endpoints (growth and reproduction endpoints) from the ECO-SSL (34.8 mg Cu/kg BW/day)

NOAEL = 18.4 mg Cu/kg BW/day

LOAEL = 34.8 mg Cu/kg BW/day

Lead

At the direction of USEPA, studies of lead effects on growth and reproduction in birds evaluated in the development of ECO-SSLs were the basis for lead TRVs in the BERA. The NOAEL was based on the geometric mean of reproduction and growth NOAEL endpoints from these studies (10.9 mg Pb/kg BW/day); the LOAEL was based on the geometric mean of LOAEL endpoints (44.6 mg Pb/kg BW/day).

NOAEL = 10.9 mg Pb/kg BW/day

LOAEL = 44.6 mg Pb/kg BW/day

Manganese

Based on work by Laskey and Edens (1985), Sample et al. (1996) from ORNL calculated a NOAEL of 977 mg Mn/kg BW/day. Applying the NOAEL-LOAEL uncertainty factor of 5 (Lewis et al. 1990), this is a NOAEL of 4,885 mg Mn/kg BW/day.

NOAEL = 977 mg Mn/kg BW/day

LOAEL = 4885 mg Mn/kg BW/day

Mercury

Only one study for inorganic mercury that used a reproductive endpoint is available. Hill and Schaffer (1976) fed Japanese quail a dose of 0.45 mg Hg/kg BW/day for 1 year that included the reproductive cycle and found no adverse effects on egg production, fertility, or hatchability of the eggs produced. The LOAEL from this study was 0.91 mg Hg/kg BW/day.

NOAEL = 0.45 mg Hg/kg BW/day

LOAEL = 0.91 mg Hg/kg BW/day

Selenium

The avian TRV (NOAEL=0.4 mg/kg BW/day and LOAEL=0.8 mg/kg BW/day) for birds exposed to selenium is based on a series of studies by Heinz and others on mallard ducks. The form of selenium tested is selenomethionine (SeM), a product of microbial metabolism, rather than either selenate or selenite. Heinz et al. (1989) reported that adult mallards suffered reduced reproductive success when fed a diet containing 8 mg SeM/kg, but that no effects were found at 4 mg SeM/kg. The resulting NOAELs and LOAELs were calculated by Sample et al. (1996) as 0.4 and 0.8 mg SeM/kg BW/day, respectively. Similar sensitivities have been shown for chickens, quail, and pheasants. These TRVs will be used for the black duck.

NOAEL = 0.4 mg Se/kg BW/day

LOAEL = 0.8 mg Se/kg BW/day

However, there appears to be good evidence that SeM effects on Anseriformes (such as the black duck) and Galliformes (chicken-like birds) may not be representative of insectivorous species such as the tree swallow.

The following information describes the adjustments to the mallard TRV that will be applied to the food chain models to compensate for differences in species sensitivity between mallard ducks and the tree swallow.

Reproductive success is generally considered one of the most sensitive measurement endpoints for studies of potential adverse effects to receptor populations. Studies have shown that the selenium content of eggs is the best estimator of reproductive success in a variety of bird species

(Fairbrother et al. 1999; Adams et al. 2003). Heinz et al. (1987; 1989) showed that the effects threshold concentration for mallard eggs is about 3 mg Se/kg dry weight. However, both laboratory and field studies have shown that black-crowned night heron, screech owl, and American kestrel accumulate egg selenium concentrations much greater than 3 mg Se/kg dry weight without adverse effects on reproduction. Furthermore, field studies have shown much higher egg selenium concentrations have no adverse effects on reproductive success in American dipper, spotted sandpiper (Harding et al. 2005), loggerhead shrike, Northern harrier (Santolo and Yamamoto 1999), and barn swallow (King et al. 1994). These studies considered together suggest that the TRV for carnivorous birds should be adjusted upwards. Probably the most relevant study for the tree swallow is that conducted with barn swallows. King et al. (1994) reported no adverse effects on reproduction with barn swallow eggs containing up to 12 mg Se/kg egg. If it is assumed that the barn swallow and tree swallow are equally sensitive, and that swallows are a good representative of an insectivorous bird feeding on emergent insects, the difference in apparent toxicity thresholds (the NOAEL) between mallard and tree swallow can be estimated as:

$$NOAEL_{swallow} = NOAEL_{mallard}\ x \left[\frac{NOEC_{swallow\ egg}}{NOEC_{mallard\ egg}}\right] = 0.4\ x\ \frac{12}{3} = 1.6\ mg\ Se\ /\ kg\ BW\ /\ day.$$

In this BERA a factor of 5 has been applied to convert a NOAEL to a LOAEL (Section 5.1.31) when a LOAEL is not available. However for this conversion we can use the same relationship between the NOAEL and LOAEL as was found in the Heinz et al. (1989) study. Assuming the same relationship holds for effect concentrations (i.e., the LOAEL is twice the NOAEL), the swallow LOAEL would be 3.2 mg Se/kg BW/day.

Thallium

No avian toxicity data for thallium was found.

Zinc

Four studies were evaluated. The NOAEL selected for zinc is based on the minimum daily requirement (MDR) for laying hens (NAS 1994). NAS reported that the MDR is 44.4 mg Zn/kg diet at 90% dry weight. In order to obtain this concentration in plants at 100% dry weight the soil-to-plant uptake equation of Efroymson et al. (2001) was used. The soil concentration that provides the MDR is 54 mg Zn/kg, which is slightly lower than the estimated arithmetic mean soil zinc concentration of 60 mg Zn/kg for the conterminous United States (Shacklette and Boerngen 1984). Applying the soil- to-worm uptake equation for zinc (Sample et al. 1999) and the allometric ingestion rate for the robin (Nagy 2001) results in a dose of 54.4 mg Zn/kg BW/day. This was assumed to be a conservative estimation of the NOAEL. The LOAEL was taken from a study by Stahl et al. (1990). These authors fed 48, 228, or 2028 mg Zn/kg food to adult leghorn chickens for 44 weeks and found a slight decrease (i.e., LOAEL) in hatchability at 131 mg Zn/kg BW/day.

NOAEL = 54.4 mg Zn/kg BW/day

LOAEL = 131 mg Zn/kg BW/day

The other studies reviewed resulted in reported NOAELs that result in unfeasible soil concentrations (Stahl et al. 1990; Jackson et al. 1986) and examined shorter exposure durations (Gasaway and Buss 1972).

Table 5-4. Summary of Avian Toxicity Reference Values (TRVs).

Analytes	Avian Receptors			
	Chronic NOAEL[a] (mg/kg-bw/d)	Chronic LOAEL[b] (mg/kg-bw/d)	Test Animal	Source
Metals				
Antimony	NA	NA	--	--
Barium	208.3	416.5	1-d old chicks	Johnson et al. 1960
Cadmium	1.47	6.3	Geometric Mean	USEPA 2005a
Copper	18.4	34.8	Geometric Mean	USEPA 2005a
Lead	10.9	44.6	Geometric Mean	USEPA 2005a
Manganese	977	4885	1-d old Japanese quail	Laskey and Edens 1985
Mercury	0.45	0.91	Japanese quail	Hill and Schaffer 1976
Selenium	0.4	0.8	Mallard[c]	Heinz et al. 1989
Thallium	NA	NA	--	--
Zinc	54.4	131	Chicken	Stahl et al. 1990
Organic Compounds				
Total PAHs & VOCs	16.1 / 161	NA	mallard	Patton and Dieter 1980
Benzene	NA	NA	--	--
Ethylbenzene	NA	NA	--	--
Toluene	NA	NA	--	--
Xylenes (total)	NA	NA	--	--
m & p-cresols	NA	NA	--	--
o-cresol	NA	NA	--	--
Trimethylbenzenes (total)	NA	NA	--	--

Notes:

a, NOAEL is no observable adverse effects level.
b, LOAEL is low observable adverse effects level.
c, Mallard-based TRV is multplied by correction factors of 4.0 for tree swallow.
d, Lower TRV for p-cresol selected as a conservative TRV for m & p-cresols.
-- Appropriate data are not available from published literature to derive NOAEL and LOAEL values.
NA, Toxicity Reference Value not available.

5.1.4.4 Mammals

The following TRVs were derived for metals and summarized in Table 5-5.

Antimony

The geometric mean of NOAEL values reported for reproduction and growth endpoints in the studies used to derive the ECO-SSL (13.3 mg Sb/kg BW/day) was used as the mammalian NOAEL for antimony. The geometric mean of the limited number of LOAEL values available from ECO-SSL studies (2.8 mg Sb/kg BW/day) was lower than the geometric mean of NOAEL values. Given the incongruous LOAEL endpoints based on a limited dataset, no LOAEL was estimated for mammals exposed to antimony.

NOAEL = 13.3 mg Sb/kg BW/day

Barium

At the direction of USEPA, the mammalian NOAEL for barium is based on the geometric mean of NOAEL endpoints from reproduction and growth studies used to derive ECO-SSLs (51.8 mg Ba/kg BW/day; USEPA 2005a). The geometric mean of LOAEL endpoints for reproduction and growth from the ECO-SSL (82.7 mg Ba/kg BW/day) is presented as the LOAEL.

NOAEL = 51.8 mg Ba/kg BW/day

LOAEL = 82.7 mg Ba/kg BW/day

Cadmium

USEPA (2005a) evaluated studies of cadmium effects on reproduction and growth in mammals in the development of ECO-SSLs. The geometric mean NOAEL from these studies was 0.77 mg Cd kg BW/day and, as directed by USEPA, represents the NOAEL for the BERA; the geometric mean of LOAEL endpoints from these studies is 6.9 mg Cd/kg BW/day and represents the LOAEL for the BERA.

NOAEL = 0.77 mg Cd/kg BW/day

LOAEL = 6.9 mg Cd/kg BW/day

Copper

Mammalian TRVs for copper were based on growth and reproduction studies used to derive ECO-SSLs (USEPA 2005a). The NOAEL was based on the geometric mean of NOAELs from these studies (23.7 mg Cu/kg BW/day); the LOAEL was based on the geometric mean of LOAEL endpoints (82.7 mg Cu/kg BW/day).

NOAEL = 23.7 mg Cu/kg BW/day

LOAEL = 82.7 mg Cu/kg BW/day

Lead

The mammalian NOAEL for lead (40.7 mg Pb/kg BW/day) was calculated as the geometric mean of growth and reproduction NOAEL from studies used to derive ECO-SSLs (USEPA 2005a). The LOAEL (182.4 mg Pb/kg BW/day) was calculated as the geometric mean of LOAEL endpoints for reproduction and growth from studies evaluated in the development of ECO-SSLs.

NOAEL = 40.7 mg Pb/kg BW/day

LOAEL = 182.4 mg Pb/kg BW/day

Manganese

Based on work by Laskey et al. (1982), Sample et al. (1996) from ORNL calculated a mammalian NOAEL of 88 and a LOAEL of 284 mg Mn/kg BW/day.

NOAEL = 88 mg Mn/kg BW/day

LOAEL = 284 mg Mn/kg BW/day

Mercury

Three studies were evaluated. The NOAEL selected for mercury is based on results from a study by Revis et al. (1989). Revis et al. (1989) reported a 20-month NOAEL of 13.2 mg Hg/kg BW/day for lethality that included 6-month estrous-cycle assessment on reproduction in mice exposed to mercuric chloride. This is proposed as the NOAEL. No LOAEL was available from the Revis et al. (1989) study, but in another study Fitzhugh et al. (1950) reported a 2-year LOAEL of 56 mg Hg/kg BW/day for growth in rats exposed to mercuric chloride. This is proposed as the LOAEL. The third study reviewed was one by Aulerich et al. (1974), which examined only a single, lower, no effect dose for a shorter time period.

NOAEL = 13.2mg Hg/kg BW/day

LOAEL = 56 mg Hg/kg BW/day

Selenium

Three chronic-term studies with reproductive endpoints were evaluated. The NOAEL selected was based on the study by Rosenfeld and Beath (1954). Other studies used only a single dose and did not produce a NOAEL (Schroeder and Mitchener 1971), or used a shorter exposure duration and did not measure reproductive success (NTP 1994).

Rosenfeld and Beath (1954) exposed pregnant rats to 0.21, 0.35, or 1.05 mg Se/kg BW/day (as potassium selenate in drinking water) and reported no adverse effects on the number of normal litters at 0.35 mg/kg BW/day in the first generation. Therefore:

NOAEL = 0.35 mg Se/kg BW/day

LOAEL = 1.05 mg Se/kg BW/day

Thallium

Four studies were available and all were evaluated. The NOAEL selected for thallium is based on a study by U.S. EPA (1986) and used by IRIS as the NOAEL for the protection of human health. Other studies were of shorter duration at a single dose level (Formigli et al. 1986), evaluated only mortality (Downs et al. 1960) or mortality and neural histology (Manzo et al. 1983).

U.S. EPA (1986) exposed rats to thallium sulfate at doses of 0, 0.008, 0.04, or 0.20 mg Tl/kg BW/day for 90-days and reported no adverse effects on body weight, organ weight, hematology or clinical chemistry, food consumption of histopathologic lesions at the highest dose tested (the only adverse effect found was alopecia or hair loss). Since rats reproduce with 8-10 weeks of birth, this is a chronic NOAEL for ecological receptors. The LOAEL was estimated by multiplying the NOAEL by 5 (Lewis et al. (1990).

NOAEL = 0.2 mg Tl/kg BW/day

LOAEL = 1.0 mg Tl/kg BW/day

Zinc

Four studies were evaluated. The NOAEL selected for zinc is based on results reported by Schlicker and Cox (1968), and Aulerich et al. (1991). Schlicker and Cox (1968) fed rats zinc oxide for 16-days during gestation and found no adverse effects on mating, fertilization, implantation, and fetal development at 160 mg Zn/kg BW/day. The LOAEL from this study was 320 mg Zn/kg BW/day. However, in another study with mink, Aulerich et al. (1991) reported that concentrations of 0, 500, 1000, or 1500 mg Zn/kg food caused no adverse effects on body weight, food consumption, haematological parameters, or histological lesions in the pancreas, liver, or kidney after 144-days. For mink the highest concentration in this study (1500 mg Zn/kg food is equivalent to a NOAEL of 205 mg Zn/kg BW/day.

Since the NOAEL from the Schlicker and Cox (1968) is lower this will be used along with the LOAEL from the same study.

NOAEL = 160 mg Zn/kg BW/day

LOAEL = 320 mg Zn/kg BW/day

Other studies reached similar NOAEL conclusions (Ketcheson et al. 1969; Maita et al. 1981, Aughey et al. 1977) but did not provide LOAEL values.

VOCs

Benzene

Three toxicity studies examining reproduction and development were evaluated. The NOAEL was based on a study by Nawrot and Staples (1979).

Nawrot and Staples (1979 exposed mice by gavage to 0.3, 0.5, or 1 ml benzene/kg BW/day from days 6 to 12 of gestation. Adverse effects on maternal mortality, and embryonic resorption were found at the lowest concentration. Therefore, the LOAEL is:

$$0.3 \text{ ml benzene/kg BW}^{-day} \times 0.8787 \text{ g/ml} \times 1000 \text{ mg/g} = 264 \text{ mg benzene/kg BW/day.}$$

This LOAEL was converted to a NOAEL by applying an extrapolation factor of 5. Therefore, the NOAEL for ingestion of benzene is:

NOAEL = 264 mg benzene/kg BW/day divided by 5

= 52.8 mg benzene/kg BW/day

The other studies evaluated a single higher effect dose of 1000 mg benzene/kg BW/day (Exxon 1986), or evaluated endpoints that are not related to population stability and provided no study protocol, few study details, and no statistical analyses (Wolf et al. 1956).

m, o, and p-Cresol

ATSDR (1992) summarized the available data concerning the toxicity of cresols to mammals. The lowest NOAELs having implications for animal population stability were:

m-cresol

ATSDR (1992) cited BRCC (1988) as reporting a NOAEL for rabbits exposed during days 6 to 15 of gestation. The rabbit NOAEL for development and reproduction is 100 mg m-cresol/kg BW/day. This is the lowest NOAEL reported.

NOAEL = 100 mg m-cresol/kg BW/day

o-cresol

ATSDR (1992) cited Hornshaw et al. (1986) 6-month feeding studies with mink and reports a NOAEL of 105 mg o-cresol/kg BW/day. Sample et al. (1996) cite the same study, but calculated a NOAEL of 219 mg o-cresol/kg BW/day. The lower estimate was selected as the NOAEL for this BERA. Other studies with o-cresol were found in ATSDR (1992), but the mink values were the lowest and mink is a Site-specific receptor.

NOAEL = 105 mg o-cresol/kg BW

p-cresol

ATSDR (1992) cited MBA (1988) as reporting that a dose of 50 mg p-cresol/kg BW/day caused nephropathy in rats after 13-weeks of dietary exposure. This is the lowest value reported in ATSDR (1992). Therefore, the NOAEL for ingestion of p-cresol is:

NOAEL = 50 mg p-cresol/kg BW/day divided by 5

= 10 mg p-cresol/kg BW/day

Ethylbenzene

Three studies of ethylbenzene toxicity were evaluated. The NOAEL was based on the study by Wolf et al. (1956). Wolf et al. (1956) exposed rats to 13.6, 136, 408, or 680 mg ethylbenzene/kg BW/day by gavage 5-days/week for 182 days. No effects on liver or kidney weight and no histological changes were found at 136 mg ethylbenzene/kg BW/day. This NOAEL was converted to a 7 day per week NOAEL by multiplying by 5/7:

$$\text{NOAEL} = 136 \text{ mg ethylbenzene/kg BW}^{\text{-day}} \text{ x } 5/7\text{-days}$$

$$= 97 \text{ mg ethylbenzene/kg BW/day.}$$

Other studies examined higher lethal doses (Smyth et al. 1962) or fewer doses with no statistical analyses (Ungvary 1986).

Toluene

Eight studies of toluene effects on reproductive or developmental endpoints were evaluated. The NOAEL was based on the study by Nawrot and Staples (1979).

Nawrot and Staples (1979) exposed mice to toluene to 0.3, 0.5, or 1.0 ml toluene three-times per day for 10 days between days 6 and 15 of gestation. They found increased mortality at the lowest concentration tested. Therefore, the LOAEL is:

$$0.3 \text{ ml toluene/kg BW}^{\text{-day}} \text{ x 3 doses/day x 0.866 g/ml} = 779 \text{ mg toluene/kg BW/day.}$$

This was converted to a NOAEL by dividing by 5. This results in a NOAEL for ingestion of benzene of:

$$\text{NOAEL} = 779 \text{ mg toluene/kg BW/day divided by 5}$$

$$= 156 \text{ mg toluene/kg BW/day.}$$

Other studies reported higher NOAELs (Smith 1983; Seidenberg et al. 1982; NTP 1990) or LC50s only (Kimura et al. 1971; Smyth et al. 1969; Withey and Hall 1975; Wolf et al. 1956).

Trimethylbenzenes

No adequate studies of the toxicity of trimethylbenzenes (TMB) were found in the literature. USEPA (1994) reported only one study of the oral toxicity of trimethylbenzenes. They reported that rats given 1,2,4-trimethylbenzene at a dose of 0.5 g/kg BW/day five days a week for four weeks died and that one rat given 0.2 g/kg BW/day died. No other data were provided. When queried for trimethylbenzene, the USEPA database IRIS (2003) provides an oral RfD based on an NTP (1986) study of xylenes. The NTP study exposed F344/N rats and B6C3F1 mice to xylenes (60% m-xylene, 13.6% p-xylene, 9.1% o-xylene, and 17% ethylbenzene) by gavage 5-days per week for 103 weeks. The NOAEL for rats, upon which the RfD was calculated is 250 mg/kg BW/day and the LOAEL is 500 mg/kg BW/day. There were no effects on mice except for hyperactivity following the daily gavage administration. The NOAEL and LOAEL for mice were 500 and 1000 mg/kg BW/day, respectively (IRIS 2003).

In the BERA, the more conservative of the two endpoints from NTP (1986) will be used to represent the TRVs for trimethylbenzene:

NOAEL= 250 mg TMB/kg BW/day

LOAEL= 500 mg TMB/kg BW/day

Xylene

Three studies of the effect of xylenes ingestion were evaluated. The NOAEL for ingestion of xylenes was taken from the study by NTP (1986).

NTP (1986) exposed rats and mice to 250, 500, or 1000 mg xylenes by gavage, 5 days per week for 13 and 103 weeks. They reported no adverse effects on histological change in reproductive organs of rats and mice, respectively, at doses of 500 and 1000 mg xylenes/kg BW/day. This NOAEL was converted to a 7 day per week NOAEL by multiplying by 5/7:

NOAEL = 500 mg xylenes/kg BW/day x 5/7

= 357 mg xylenes/kg BW/day.

Other studies reported NOAELs at lower doses (Seidenberg et al. 1986; Marks et al. 1982).

Table 5-5. Summary of Mammalian Toxicity Reference Values (TRVs).

Analytes	Mammalian Receptors			
	Chronic NOAEL[a] (mg/kg-bw/d)	Chronic LOAEL[b] (mg/kg-bw/d)	Test Animal	Source
Metals				
Antimony	13.3	NA	Geometric Mean	USEPA 2005a
Barium	51.8	82.7	Geometric Mean	USEPA 2005a
Cadmium	0.77	6.9	Geometric Mean	USEPA 2005a
Copper	23.7	82.7	Geometric Mean	USEPA 2005a
Lead	40.7	182.4	Geometric Mean	USEPA 2005a
Manganese	88	284	rat	Laskey et al. 1982
Mercury	13.2	56	mouse/rat	Revis et al. 1989 (NOAEL); Fitzhugh et al. 1950 (LOAEL)
Selenium	0.35	1.05	rat	Rosenfeld and Beath 1954
Thallium	0.2	1	rat	USEPA 1996
Zinc	160	320	rat	Schlicker and Cox 1968
Organic Compounds				
Total PAHs & VOCs	129	NA	rat	Shopp et al 1984; Plasterer et al 1985
Benzene	52.8	264	mouse	Nawrot and Staples 1979
Ethylbenzene	97	NA	rat	Wolf et al 1956
Toluene	156	779	mouse	Nawrot and Staples 1979
Xylenes (total)	357	NA	rat	NTP 1986
m & p-cresols	10	NA	rat	MBA 1988[d]
o-cresol	21	NA	mink	MBA 1988
Trimethylbenzenes (total)	250	500	rat	IRIS 2003

Notes:
a, NOAEL is no observable adverse effects level.
b, LOAEL is low observable adverse effects level.
c, Mallard-based TRV is multplied by correction factors of 4.0 for tree swallow.
d, Lower TRV for p-cresol selected as a conservative TRV for m & p-cresols.
-- Appropriate data are not available from published literature to derive NOAEL and LOAEL values.
NA, Toxicity Reference Value not available.

5.2 EXPOSURE ANALYSIS

In the exposure analysis the relationship between receptors at the Site and COPCs are evaluated. The information necessary to estimate exposure is described in this section, including an overview of the various sources, the spatial and temporal distribution of chemical stressors, and the methods through which different types of exposure are estimated for each receptor group.

5.2.1 Calculation of Exposure Point Concentrations

EPCs used to estimate exposure were calculated as the UCL_{95}. Since calculation of the UCL_{95} is dependent on the underlying distribution of sample data the distribution was tested for normality using ProUCL (USEPA 2004). For normally distributed datasets (α=0.05), the UCL_{95} was calculated based on the Student's t-distribution (USEPA 2000):

$$UCL_{95} = X + t_{\alpha,n-1} SD / \sqrt{n}$$

where:

UCL_{95} = 95 percent confidence limit of the arithmetic mean

X = arithmetic mean concentration of the data (non-detections estimated as 50 percent of the method detection limit)

SD = standard deviation of the data (non-detections estimated as 50 percent of the method detection limit)

$t_{\alpha,n-1}$ = Student's t-statistic at $\alpha = 0.05$

n = sample size

Constituents with non-normal distributions were calculated using a bootstrap or jackknife resampling procedure. The major advantage of these methods is they can provide a robust approximation of the UCL without having to make assumptions regarding an underlying distribution to the data (EPA 1997). Either of these methods can be used; however, the Jackknife method tends to be more robust and more conservative (and thus preferred) on datasets with fewer samples (e.g., sample sizes less than 15). When analysis with ProUCL indicated that the underlying distribution was not normal, the Standard Bootstrap UCL_{95} was used. If the Standard Bootstrap was not available then the Jackknife UCL_{95} was used.

Bootstrapping is a nonparametric statistical technique that draws repeated random samples of size *n* with replacement from the original set of data. A sample mean is calculated with each replacement, resulting in a new population of sample means. In this assessment, standard bootstrapping techniques were used to produce a new population of 1000 sample means. The central limit theorem states that arithmetic means obtained from independent, random samples drawn from the same population will be approximately normally distributed, regardless of the distribution of the sampled population, if the sample size is large (USEPA 2002). Therefore, the principals of the Student's t-distribution may be applied to the bootstrap estimates of the mean to calculate a UCL_{95} based on normally distributed data:

$$UCL_{95} = X_r + SD_r \times 1.645$$

where:

UCL_{95}	= 95 percent confidence limit of the arithmetic mean
X_r	= mean of bootstrapped estimates of the mean
SD_r	= standard deviation of the bootstrapped estimates
1.645	= Student's t-statistic for degrees of freedom greater than 120 at α equal to 0.05

For the jackknife mean and standard error are calculated as follows:

Step 1: n pseudovalues (ϕ) are first calculated by leaving out each of the observations i in turn:

$$\phi = (n \times \overline{X}) - [(n-1) \times \overline{X}_{i-1}]$$

Step 2: The jackknifed estimate of the mean is then:

$$\Phi = \sum(\phi) \div n$$

Step 3: The standard error of the mean is calculated as:

$$SE_{mean} = \sqrt{\Sigma(\phi_i - \Phi)^2 / [n \bullet (n-1)]}$$

Step 4: The upper confidence limit of the jackknifed mean is calculated as:

$$UCL_{\alpha} = \Phi + t_{1-\alpha,n-1} \bullet SE_{mean}$$

EPCs calculated for sediment and soil exposure media are presented for terrestrial and aquatic exposure areas in Appendix I.

Because the UCL_{95} of the data represents a reasonable maximum exposure for ecological receptors the UCL_{95} was then compared to the screening criteria. This has the effect of eliminating extreme but unrepresentative environmental concentrations. Table 5-6 summarizes those COPCs whose UCL_{95} exceeded the screening criteria.

Table 5-6. List of Site Contaminants Whose EPC based upon the 95%UCL Exceeds the Screening Criteria.

Surface Water	Sediment	Soil
None	Total PAHs	Total PAHs
	Dibenzofuran	Antimony
	m-Cresol	Cadmium
	o-Cresol	Lead
	p-Cresol	Manganese
	1,2,4-Trimethylbenzene	Mercury
	1,3,5-Trimethylbenzene	Selenium
	Benzene	Zinc
	Ethylbenzene	
	Toluene	
	Total Xylenes	
	Barium	
	Copper	
	Selenium	
	Thallium	

5.2.2 Exposure Estimation for Birds and Mammals

Exposure estimates for birds and mammals were calculated using food chain models. Simplified food chain models were developed to calculate average daily doses (ADDs) of COPCs that selected receptor groups experience through exposure to sediment and surface soil at the Site.[15] The ADD represents the dose of a chemical that a receptor may ingest if it foraged exclusively within the boundaries of the Site. ADDs for wildlife receptors are calculated using (1) exposure-point concentrations for prey and media, and (2) receptor-specific exposure parameters and food chain model assumptions (Appendix F). These ADDs can then be compared to toxicity reference values (TRVs), which represent no observable adverse effects levels (NOAELs) or lowest observable adverse effects levels (LOAELs). Appendix F provides a detailed description of the calculation of ADDs, including the derivation of exposure parameters, biota accumulation factors (BAFs), biota-sediment accumulation factors (BSAFs), and bioavailability adjustments. For all receptors an area use factor (AUF) of 100% is used to calculate the ADD for each of the modelled receptors. This is a very conservative assumption for wildlife receptors that have significantly larger foraging areas than the approximately 10 acre Site.

[15] Exposure through surface water was not considered in the wildlife models because no COPCs were detected in surface water samples.

The simplified food chain model considers the primary routes of exposure to wildlife receptors: the direct ingestion of prey and the incidental ingestion of soil or sediment. There were only occasional low level detections of benzene, ethylbenzene, toluene and naphthalene in the filtered fraction of Site surface water and none of these detections exceeded screening criteria. No other VOCs or PAHs were detected. For this reason the surface water exposure pathway will not be used in the wildlife models.

Chemical concentrations in prey are expressed as a function of the chemical concentrations in sediment, or soil, using BAFs for terrestrial prey items and BSAFs for aquatic prey items. Other important parameters in the model include, receptor body weight, and food ingestion rates.

The total dose (ADD_{total}) experienced by each selected receptor is the sum of the doses obtained from the three primary routes of exposure:

$$ADD_{total} = ADD_{diet} + ADD_{substrate}$$

In the model, the total dose from each route of exposure is calculated individually as follows:

Dietary Dose:

$$ADD_{diet} = \frac{IR_{diet} \times \sum (C_{food} \times DF_i)}{BW}$$

where:

ADD_{diet}	= Dose of COPC obtained from the diet (mg COPC/kg receptor body weight-day)
IR_{diet}	= Ingestion rate of food (kg food ingested per day, dry weight)
C_{food}	= Concentration of COPCs in food item *i* (mg COPC/kg food item, dry weight); Determined using direct measurements of tissue concentrations or estimated using bioaccumulation factors (BAFs) or biota-sediment accumulation factors (BSAFs) (See Section 5.2.3).
DF_i	= Dietary fraction of food item *i* (proportion of food type in the diet)
BW	= Body weight of the receptor, wet weight (kg)

Substrate Dose:

$$ADD_{substrate} = \frac{IR_{substrate} \times C_{substrate}}{BW}$$

$ADD_{substrate}$	= Dose of COPC obtained from soil or sediment (mg COPC/kg receptor body weight-day)
IR_s	= Incidental Ingestion Rate of soil (kg substrate ingested per day, dry weight)
$C_{substrate}$	= Mean or UCL_{95} COPC concentration in substrate (mg COPC/kg substrate, dry weight)
BW	= Body weight of the receptor, wet weight (kg)

The receptor dose of COPCs from diet, and incidental substrate ingestion is modeled using dry weight parameters. To avoid introducing unnecessary uncertainty into the model by converting parameters from dry weight to wet weight based on approximate moisture contents of dietary items, model parameters for food ingestion rates, substrate ingestion rates, and substrate-to-biota accumulation rates also are expressed on a dry weight basis.

5.2.3 Estimates of Dietary Exposure Point Concentrations for Wildlife

The concentration of Site COPCs in prey consumed eaten by wildlife was estimated in one of three manners:

1) Tissue concentrations of organisms (wild fish) actually collected on Site;
2) Tissue concentrations of the invertebrate benthic worm, *L. variegatus*, that resulted from the bioaccumulation bioassay; or
3) Using literature based BAFs and BSAFs and applying it to levels of COPCs in soil or sediment to estimate levels of COPCs expected in wildlife prey.

During the RI, tissue concentrations were measured in two categories of prey: fish and benthic invertebrates. Fish were collected in Site water at two different times and levels of COPCS were quantified in species representative of likely wildlife prey: smelt, brown bullhead and smallmouth bass. Appendix C describes this investigation and summarizes the data resulting from it. Estimates of tissue concentrations of benthic invertebrates were developed from the *L. variegatus* bioaccumulation study. It was assumed that under the test conditions, this soft-bodied infaunal oligochaete would provide a very conservative estimate of COPCs in benthic invertebrates and thus maximize the dose to wildlife feeding on aquatic invertebrates. Appendix B describes the bioaccumulation study and summarizes the data resulting the investigation. The fish and worm data were used to estimate a UCL_{95} body burden concentration in these species (Appendix I) that is used in the wildlife dose rate modeling (Appendix F).

5.2.3.1 Doses for Wildlife from Benthic Invertebrates and Fish

From Benthic Invertebrates

Doses to invertivorous wildlife, i.e., tree swallow, big brown bat, and black duck[16] were calculated using concentrations of PAHs measured in the freshwater benthic worm, *L. variegatus*, chronically exposed to Site sediments in the laboratory. BSAFs for PAHs were calculated as the ratio of the lipid normalized concentrations of PAHs in *L. variegatus* to the organic carbon normalized concentrations of PAHs in the bioassay sediments. Normalized[17] BSAFs for 23 individual PAHs evaluated in the 17 samples included in the 28-day *L. variegatus* bioaccumulation study (Table 5-7). These BSAFs were then used to estimate the Site-wide

[16] For the purposes of the BERA, it was assumed that the black duck feeds exclusively on benthic macroinvertebrates

[17] 'Normalized BSAFs' refers to BSAFs normalized by the geometric mean lipid fraction of *L. variegatus* and the geometric mean organic carbon fraction in the test sediment from the 28-day bioaccumulation study.

UCL_{95} concentration of benthic invertebrates inhabiting the Site. This was accomplished in two steps as follows.

1) Site-wide BSAFs were calculated for each individual PAH compound from the bioaccumulation study stations using the normalized BSAFs based on the UCL_{95} concentration of sediment organic carbon calculated for the Site area and the geometric mean lipid concentration measured in the bioaccumulation study. Site-wide BSAFs were calculated for each compound as follows:

$$BSAF_{Site-Wide} = BSAF_{norm} \times f_{lipid} \div f_{oc}$$

where: $BSAF_{Site-Wide}$ = BSAF based on Site-wide fraction of sediment organic carbon and geometric mean estimated lipid fraction in the worms ;

$BSAF_{norm}$ = Normalized BSAF for each individual PAH compound (kg sediment organic carbon / kg lipid);

f_{lipid} = Fraction of lipids (0.0785, geometric mean calculated for *L. variegatus* on a dry weight basis); and

f_{oc} = Site-wide fraction of sediment organic carbon (0.1857, UCL_{95} calculated from sediment samples in the Site area).

2) Concentrations of PAHs in Site-wide prey were estimated by multiplying the Site-wide BSAF by the Site-wide UCL_{95} sediment concentration:

$$C_p = BSAF_{Site-Wide} \times C_s$$

where: C_p = Estimated concentration of PAHs in prey (mg PAH/kg prey, dry weight)

$BSAF_{Site-wide}$ = BSAF based on Site-wide fraction of sediment organic carbon and estimated lipid fraction in benthic invertebrates; and

C_s = Concentration of PAH in sediment (mg PAH/kg sediment, dry weight)

The 28-day *L. variegatus* bioaccumulation study did not analyze the concentrations of dibenzofuran or the VOCs that were identified as COPCs in the BERA: benzene, m, p and o-cresols, ethylbenzene, toluene, and total xylenes. In addition, since biphenyl was analyzed in fish, but not in worms, it was felt that the concentration of that compound should also be estimated. The normalized BSAF developed for acenaphthene from the *L. variegatus* bioaccumulation study was used to estimate concentrations of dibenzofuran and biphenyl in benthic invertebrate tissue due to similar log K_{ow}s and molecular weights between compounds. The normalized BSAF for naphthalene was used as a conservative surrogate to estimate concentrations of VOCs in benthic invertebrates based on the assumption that VOCs do not bioaccumulate at a greater rate than naphthalene (Table 5-7, Roubal et al. 1977).

Table 5-7. Estimation of BSAFs Based on 28-day *L. variegatus* Bioaccumulation Study

Compound	Log K_{ow}	Normalized BSAFs (kg sediment organic carbon / kg lipid)			
		Minimum	Geometric Mean	UCL_{95}	Maximum
1-Methylnaphthalene	3.84	0.01	1.01	4.09	9.26
1-Methylphenanthrene	5.04	2.40	9.31	38.2	124.78
2,3,5-Trimethylnaphthalene	4.86	0.91	6.80	18.23	49.42
2,6-Dimethylnaphthalene	4.37	0.14	2.96	8.33	25.87
2-Methylnaphthalene	3.86	0.01	1.43	5.72	19.17
Acenaphthene	4.01	0.07	1.27	4.37	13.80
Acenaphthylene	3.22	0.46	3.44	10.49	33.36
Anthracene	4.53	0.47	3.02	10.29	27.36
Benzo(a)anthracene	6.71	1.70	6.38	23.07	66.60
Benzo(a)pyrene	6.11	0.55	3.31	12.15	40.86
Benzo(b)fluoranthene	6.27	0.93	5.63	23.18	64.01
Benzo(e)pyrene	6.14	2.26	7.31	24.59	73.04
Benzo(g,h,i)perylene	6.51	0.66	2.71	8.45	22.87
Benzo(k)fluoranthene	6.29	2.35	9.01	27.62	86.32
Chrysene	5.71	2.45	7.32	25.52	80.35
Dibenzo(a,h)anthracene	6.71	1.64	7.69	22.15	56.19
Fluoranthene	5.08	1.84	7.18	28.08	88.26
Fluorene	4.21	0.17	2.42	7.95	26.69
Indeno(1,2,3-cd)pyrene	6.72	0.28	1.95	6.69	18.69
Naphthalene	3.36	0.02	3.12	12.51	42.97
Perylene	6.14	1.65	7.01	12.49	34.56
Phenanthrene	4.57	1.34	6.87	20.42	64.80
Pyrene	4.92	2.34	7.45	37.31	106.96

Concentrations of organic compounds in benthic invertebrates estimated based on BSAFs and the UCL_{95} sediment concentrations that are used in the food chain models are presented in Appendix I, Table I-3. Exhibit 5.1 provides a sample calculation of the naphthalene concentration estimated in benthic invertebrates based on the UCL_{95} sediment concentration and BSAF. This tissue concentration substantially exceeds those measured in the lab because the bioaccumulation bioassay was not conducted using sediments from SQT1 and SQT7, which had the highest levels of PAHs on a carbon normalized basis. It is likely that applying this BSAFs to the much greater Site concentrations is very conservative.

Exhibit 5.1: Calculations of Site-wide Benthic Invertebrate Tissue Concentrations Using Biota to Sediment Accumulation Factors (BSAFs)

The concentration of naphthalene in benthic invertebrate tissue was estimated based on the BSAF determined in the 28-day *L. variegatus* bioaccumulation study and the UCL_{95} naphthalene concentration measured in sediments at the Site. The ratios of the naphthalene concentration measured in *L. variegatus* to the concentration of naphthalene measured in bioassay sediment were calculated for each of the 17 samples evaluated in the *L. variegatus* bioaccumulation study. The calculated ratios were normalized by the sediment organic carbon content (geometric mean of organic carbon measured in bioassay samples) and *L. variegatus* lipid content (geometric mean of lipid content measured in bioassay samples); the resulting values are hereafter referred to as normalized BSAFs. The geometric mean of the 17 normalized BSAFs calculated for naphthalene in the bioaccumulation samples (3.12 kg sediment organic carbon/kg lipid) was used to estimate naphthalene concentrations in benthic invertebrates at the entire Site. The geometric mean of normalized BSAFs calculated for other organic compounds are presented in Table 5-7.

The geometric mean of the normalized BSAFs for naphthalene (3.12 kg sediment organic carbon/kg lipid) derived under laboratory conditions was corrected to account for differences in sediment organic carbon content at the Site. A Site-wide BSAF was calculated using the UCL_{95} sediment organic carbon fraction (0.1857) and geometric mean lipid fraction measured in *L. variegatus* (0.0785, dry weight), as follows:

$$BSAF_{Site-Wide} = BSAF_{norm} \times f_{lipid} \div f_{oc}$$

$$BSAF_{Site-Wide} = 3.12\,(kg\,OC\,/\,kg\,lipid) \times 0.0785\,(kg\,lipid\,/\,kg\,tissue, dry\,weight) \div 0.1857\,(kg\,OC\,/\,kg\,sediment, dry\,weight)$$

$$BSAF_{Site-Wide} = 1.32\,(kg\,sediment, dry\,weight\,/\,kg\,tissue, dry\,weight)$$

The Site-wide BSAF was then multiplied directly by the measured concentration of naphthalene in sediment (UCL_{95} concentration for the Site) to estimate the Site-wide naphthalene concentrations in benthic invertebrate tissue (C_p, on a dry weight basis):

$$C_p\,(mg\,naphthalene\,/\,kg\,tissue, dry\,weight) = BSAF_{Site-Wide} \times C_s$$

$$C_p = 1.32\,(kg\,sediment, dry\,weight\,/\,kg\,tissue, dry\,weight) \times 107.47\,(mg\,naphthalene\,/\,kg\,sediment, dry\,weight)$$

$$C_p = 28.378\,(mg\,naphthalene\,/\,kg\,tissue, dry\,weight)$$

Estimated benthic invertebrate tissue concentrations calculated based on BSAFs and UCL_{95} sediment concentrations are presented in Appendix I, Table I-3.

The preceding example calculates the estimated naphthalene concentration in benthic invertebrates on a dry weight basis for use in the food chain models. However, this approach was also used to estimate benthic invertebrate body burdens as lipid-normalized molar concentrations (wet weight) for comparisons with the NEBR developed in Section 5.1. The lipid-normalized molar concentration (µmol/g lipid) for naphthalene was calculated as the lipid-normalized concentration divided by the molecular weight of naphthalene ($MW_{naphthalene}$):

$$C_p\,(\mu mol/g\,lipid) = \left(\frac{3.12\,(kg\,OC/kg\,lipid \times 107.47\,(mg\,naphthalene/kg\,sediment,dry\,weight)}{0.1857\,(kg\,OC/kg\,sediment)}\right) \div 128.19\,(g/mol)$$

$$C_p\,(\mu mol/g\,lipid) = 1807.54\,(mg\,naphthalene/kg\,lipid) \div 128.19\,(g/mol)$$

$$C_p\,(\mu mol/g\,lipid) = 1807.54\,(\mu g\,naphthalene/g\,lipid) \div 128.19\,(g/mol)$$

$$C_p\,(\mu mol/g\,lipid) = 14.1\,(\mu mol/g\,lipid)$$

Estimated lipid-normalized molar concentrations of PAHs and VOCs in benthic invertebrate tissues calculated based on UCL_{95} sediment concentrations and BSAFs are presented in Section 5.2.4 (Table 5-14).

The normalized BSAFs estimated from the 28-day *L. variegatus* bioaccumulation study were compared two other sources of BSAFs, the TLM of DiToro et al. (2000) and the U.S. Army Corps of Engineers (USACE) Environmental Residue Effects Database (ERED). DiToro et al. (2000) rearranged the TLM to predict the BSAF for PAHs:

$$BSAF = \frac{[PAH]_{lipid}}{[PAH]_{organic\ carbon}} = Kow^{-0.38}$$

and concluded that BSAFs should be less than 1.0.Table 5-8). The ERED also contains BSAFs for *L. variegatus* exposed to PAHs (Table 5-9). The BSAFs range from 0.45 for benzo(a)pyrene to 6.8 for naphthalene.

BSAFs for PAH compounds derived from field-collected tissue studies and bioaccumulation studies using field sediments were compiled from the literature for comparison with the BSAFs derived from the *L. variegatus* bioaccumulation study (Table 5-10). A limited number of field-collected tissue studies were available in the literature. Brunson et al. (1998) compiled field tissue and sediment data for *L. variegatus* from sites in the upper Mississippi River and Saint Croix River. The mean BSAFs calculated from these field datasets are on the same order as the geometric mean BSAFs calculated from the *L. variegatus* bioaccumulation study conducted in the present study. However, BSAFs derived from field measurements of tissue of other invertebrates were generally an order of magnitude or more lower than the *L. variegatus* BSAFs calculated by Brunson et al. (1998) or the current study. Gewartz et al. (2000) evaluated bioaccumulation from field-collected tissue samples of mayflies, mussels, amphipods, and crayfish and reported BSAFs less than 1.0 for these invertebrates for all measured PAHs, except naphthalene. BSAFs for naphthalene ranged from 0.706 for crayfish to 1.451 for mayflies and mussels (Table 5-10).

A review of bioaccumulation studies using field-collected sediments indicates that BSAFs for invertebrates are generally below 1.0. BSAFs derived from bioaccumulation studies using field sediments ranged from 0.002 to 1.9 (Table 5-8). BSAFs greater than 1.0 were reported for phenanthrene in two studies and fluoranthene and pyrene in one study each. The range of BSAFs based on field-collected sediments from these studies is consistent with Kraaij et al. (2001) who reported BSAFs for a marine amphipod ranging from 0.25 to 1.7 from sediments collected from contaminated harbors in the Netherlands. Lamoureux and Brownawell (1999) also reported tPAH BSAFs less than 1.5 for *Yoldia* (Bivalva) exposed to sediments collected from New York Harbor. Tracey and Hansen (1996) reported a mean BSAF of 0.34 for PAHs calculated from 4,054 field and laboratory measurements of 27 species. Other studies also reported BSAFs less than 1.0 for PAH compounds (Maruya et al. 1997; Mitra et al. 2000).

Based on comparisons with normalized BSAFs calculated by DiToro and McGrath (200b), those compiled in ERED as well as other field studies, it was concluded that the normalized BSAFs calculated from the 28-day *L. variegates* bioaccumulation study provided very conservative estimations of PAH and VOC concentrations in benthic invertebrate tissue at the Site. For most compounds, the normalized BSAFs used in this study were an order of magnitude greater than those estimated by the TLM and the preponderance of invertebrate BSAFs for PAHs reported in the literature. Normalized BSAFs developed for the BERA also were greater than those compiled in ERED.

Table 5-8. Estimation of BSAFs using Target Lipid Model (DiToro et al. 2000).

Compound	Log K_{ow}	K_{ow}	Normalized BSAF (kg sediment organic carbon / kg lipid)
1-Methylnaphthalene	3.84	6918	0.715
1-Methylphenanthrene	5.04	109648	0.643
2,3,5-Trimethylnaphthalene	4.86	72444	0.654
2,6-Dimethylnaphthalene	4.37	23442	0.682
2-Methylnaphthalene	3.86	7244	0.713
Acenaphthene	4.01	10233	0.704
Acenaphthylene	3.22	1660	0.754
Anthracene	4.53	33884	0.673
Benzo(a)Anthracene	6.71	5128614	0.556
Benzo(a)Pyrene	6.11	1288250	0.586
Benzo(b)Fluoranthene	6.27	1862087	0.578
Benzo(e)Pyrene	6.14	1380384	0.584
Benzo(g,h,i)Perylene	6.51	3235937	0.566
Benzo(k)Fluoranthene	6.29	1949845	0.577
Biphenyl	4.17	14791	0.694
Chrysene	5.71	512861	0.607
Dibenzo(a,h)anthracene	6.71	5128614	0.556
Fluoranthene	5.08	120226	0.641
Fluorene	4.21	16218	0.692
Indeno(1,2,3-cd)Pyrene	6.72	5248075	0.555
Naphthalene	3.36	2291	0.745
Perylene	6.14	1380384	0.584
Phenanthrene	4.57	37154	0.670
Pyrene	4.92	83176	0.650

Table 5-9. BSAFs for *L. variegatus* from USACE ERED Database.

Analyte	Normalized BSAF (kg sediment organic carbon/kg lipid)
Benzo(a)pyrene	0.37
Benzo(a)pyrene	0.23
Benzo(a)pyrene	0.5
Benzo(a)pyrene	0.13
Benzo(a)pyrene	1
Benzo(a)pyrene	0.5
Benzo(a)pyrene	1.34
Geometric Mean:	0.45
Benzo(a)anthracene	0.97
Chrysene	1.5
Chrysene	1.1
Geometric Mean:	1.28
Fluoranthene	1.8
Fluoranthene	1.6
Geometric Mean:	1.70
Naphthalene	5.3
Naphthalene	8.8
Geometric Mean:	6.83
Perylene	2.2
Perylene	1
Geometric Mean:	1.48
Pyrene	2.3
Pyrene	2.2
Pyrene	0.52
Pyrene	0.29
Pyrene	0.74
Pyrene	0.29
Pyrene	1.34
Pyrene	0.66
Pyrene	2.03
Geometric Mean:	0.87
2-Methyl naphthalene	2.6
2-Methyl naphthalene	6.7
Geometric Mean:	4.17

Table 5-10. Biota-Sediment Accumulation Factors for PAHs Derived From Field Collected Tissue Studies and Bioaccumulation Studies Using Field-Collected Sediment.

PAH Compound	K_{ow}	Field-Collected Tissue Studies					Bioaccumulation Studies Using Field-Collected Sediment				
	Organism:	*Lumbriculus* (Oligochaete)	Mayfly	Dreissenia (Mussel)	Amphipods	Crayfish	*Ilyodrilus* (Oligochaete)	*Lumbriculus* (Oligochaete)	*Lumbriculus* (Oligochaete)	*Nereis* (Polychaete)	*Hinia* (Gastropoda)
	Reference:	Brunson et al. (1998)	Gewartz et al. (2000)	Gewartz et al. (2000)	Gewartz et al. (2000)	Gewartz et al. (2000)	Lu et al. (2006)	Van Hoof et al. (2001)	Ingersoll et al. (2006)	Cornelissen et al. (2006)	Cornelissen et al. (2006)
	Study Location:	Upper Mississippi River and Saint Croix River	Western Lake Erie	Western Lake Erie	Western Lake Erie	Western Lake Erie	Anacostic River	Little Scioto River, Ohio	Little Scioto River, Ohio	Three Harbors in Norway	Three Harbors in Norway
	PAH Pollution:	Relatively Low	Relatively Low	Relatively Low	Relatively Low	Relatively Low	Moderate	Downstream of Creosote Source	Contaminated	Contaminated	Contaminated
Naphthalene	3.36	8.8	1.451	1.451	1.137	0.706					
2-methyl naphthalene	3.86	6.7									
Fluorene	4.21		0.267	0.067	0.283	0.033		0.38	0.95		
Anthracene	4.53							0.33	0.89		
Phenanthrene	4.57		0.165	0.099	0.146	0.019	1.55	0.28	1.6		0.01
Pyrene	4.92	2.2	1.005	0.061	0.017	0.003	0.49	0.16	1.7	0.058 - 0.11	0.015 - 0.077
Fluoranthene	5.08	1.6	0.514	0.115	0.073	0.004		0.21	1.9	0.008 - 0.028	0.007 - 0.016
Chrysene/triphenylene	5.71	1.1	0.606	0.216	0.038	0.004	0.48	0.12	0.74	0.002	0.002
Benzo(a)pyrene	6.11		0.185	0.016	0.006	0.004	0.09	0.13	0.84	0.0042 - 0.011	0.006 - 0.008
Benzo(e)pyrene	6.14									0.024 - 0.06	0.011 - 0.052
Perylene	6.14	1.02								0.0029 - 0.01	0.006 - 0.012
Benzo(b)fluoranthene	6.27		0.043	0.099	0.004	0.003				0.0057 - 0.011	0.0057 - 0.007
Benzo(k)fluoranthene	6.29						0.11				
Benzo(g,h,i)perylene	6.51		0.131	0.025	0.006	0.004				0.0036 - 0.009	0.010 - 0.018
Benzo(a)anthracene	6.71	0.5	0.347	0.088	0.010	0.007					
Dibenzo(a,h)anthracene	6.71		0.198	0.243	0.027	0.018					
Indeno(g,h,i)perylene	6.72		0.277	0.053	0.008	0.005				0.0022 - 0.010	0.008 - 0.016

Note:
"PAH pollution" refers to the relative magnitude of PAH levels in the sediment

Because concentrations of metals in aquatic benthic invertebrates were not measured, they were estimated based on BSAFs or regression models developed or obtained from the literature. The BSAF for barium was estimated as the UCL_{95} BSAF calculated from co-located sediment and tissue data reported by Hamilton and Buhl (2003a and 2003b). Concentrations of copper were estimated as the 95 percent upper prediction limit (95UPL) of regression models developed by Bechtel (1998b). Concentrations of selenium in benthic invertebrates were based on a significant regression ($p < 0.001$) of sediment and benthic invertebrate concentrations of selenium developed from co-located sediment and tissue data reported by Hamilton and Buhl (2003a and 2003b). A weighted-average of thallium BSAFs reported in Borgmann et al. (1998) for the amphipod *H. azteca* was used to estimate concentrations of thallium in benthic invertebrates.

Swallows and bats feed on emergent aquatic insects, not the immature benthic forms. Bechtel (1998b) indicates that the regression model they developed based on depurated organisms was the best estimate of adult concentrations of copper. However, correction factors were applied to estimated aquatic life stage concentrations calculated for copper, selenium, and PAHs/VOCs to the estimated concentrations present in emergent insects. For selenium, a correction factor of 0.4 was applied to concentrations in aquatic stage invertebrates to estimate concentrations in emergent stage invertebrates. This correction factor was based on Reinfelder and Fisher (1994) who found that 59.2% of ^{75}Se that was found to be bound to the exoskeleton of copepods. Reinfelder and Fisher (1994) also cite Bertine and Goldberg (1972) who reported that 61% of the selenium in shrimp was due to exoskeleton binding. Since the exoskeletons of copepods, shrimp, and aquatic insects are composed of chitin, these findings are directly applicable to insects. Assuming a similar partitioning of selenium in aquatic insects (i.e. 59.2 to 61% associated with the exoskeleton in the final molt), approximately 40% of selenium found in aquatic stage invertebrates would remain in emergent invertebrates following molting.

A correction factor of 0.135 was applied to concentrations of PAHs/VOCs estimated for aquatic life stage invertebrates to estimate concentrations in emergent insects. Bell et al. (2004) exposed fourth-instar midge larvae to fluoranthene for 72 to 96-hr. and the emergent adults were collected in traps. Larvae, exuviae, and adults tissues were collected and analyzed for fluoranthene. The larvae exhibited a concentration-dependent uptake of fluoranthene and contained significantly greater concentrations of fluoranthene than the emergent adults. In three different exposure concentrations, the emergent adults contained 0.78, 1.29, and 13.5% of the larval fluoranthene concentration and the exuviae contained more fluoranthene than the emergent adult. The highest proportion of retained fluoranthene, 13.5% was applied to the *L. variegates* data to estimate the doses received by flying insectivores at the Site. For the remaining COPCs, concentrations estimated for aquatic life stages were used to conservatively estimate concentrations for emergent life stages.

From Fish

Doses to piscivorous wildlife, i.e., osprey, double-crested cormorant, and mink, were calculated based on site-specific tissue measurements and normalized BSAFs estimated from Site data. The UCL_{95} tissue concentration of the 24 PAHs measured from all fish collected at the site was used as the exposure point concentration for total PAH concentrations in fish tissue. Site-specific tissue measurements were not available for dibenzofuran and the VOCs identified as COPCs in the BERA: benzene, m, p and o-cresols, ethylbenzene, toluene, and total xylenes. The geometric mean normalized BSAF for the 24 PAH compounds measured in fish tissue was calculated and the resultant normalized BSAF was used to calculate the concentrations of the unmeasured COPCs in fish tissue. This calculation was based on the UCL_{95} sediment concentrations of individual PAHs and the brown bullhead sample (W-3-4) containing the greatest concentrations of PAHs (Table 5-11). The geometric mean of normalized BSAFs calculated for the individual PAH compounds was 0.0146, which is an order of magnitude greater than other BSAFs that have been reported for PAHs in fish. Burkhard and Lukasewycz (2000), of U.S. EPA's National Health and Environmental Effects Research Laboratory, state that "an extensive but unsuccessful literature search was performed for field-measured bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) for polycyclic hydrocarbons (PAHs); no reported values were found for fish." The lack of BAFs and BSAFs for PAHs occurs in part because PAHs are metabolized by fish, resulting in very low or non detectable concentrations of the parent PAHs in fish tissues [Varanasi et al. 1989]. Using data from several studies Burkhard and Lukasewycz (2000) calculated BSAFs for phenanthrene (0.00011), fluoranthene (0.00016), pyrene (0.0071) benzo(a)pyrene (0.0054), and chrysene/triphenylene (0.00033).

The normalized BSAF calculated from the Site-wide fish tissue data was used to estimate fish tissue concentrations of dibenzofuran and the VOCs identified as COPCs by applying the Site-wide BSAF calculated for PAHs to Site-wide sediment concentrations of dibenzofuran and VOCs to estimate the concentrations of these unmeasured COPCs in fish tissue:

$$BSAF_{Site=Wide} = BSAF_{norm} \times f_{lipid} \div f_{oc}$$

$$C_p = BSAF_{Site-Wide} \times C_s$$

where:

$BSAF_{Site\text{-}Wide}$ = BSAF based on site-specific fraction of sediment organic carbon and measured lipid fraction in the fish ;

$BSAF_{norm}$ = Normalized BSAF for each individual PAH compound (kg sediment organic carbon / kg lipid);

f_{lipid} = Fraction of lipids (0.12, geometric mean calculated for fish measured at the site on a dry weight basis);

f_{oc} = Site-wide fraction of sediment organic carbon (0.1857, UCL_{95} concentration calculated from sediment samples in the site area).

C_p = Estimated concentration of PAHs in food/prey item (mg PAH/kg prey, dry weight); and

C_s = Concentration of PAH in sediment (mg PAH/kg sediment, dry weight)

Table 5-11. BSAF Calculated for Site Fish.

Compound	Sediment Concentration (ug/kg sediment OC)	Brown Bullhead Concentration (ug/kg lipid)	Normalized BSAF (kg sediment organic carbon/kg lipid)
1-Methylnaphthalene	18920	4166.7	0.2202
1-Methylphenanthrene	4202	541.7	0.1289
2,3,5-Trimethylnaphthalene	1928	541.7	0.2810
2,6-Dimethylnaphthalene	14233	1791.7	0.1259
2-Methylnaphthalene	295705	1375.0	0.0046
Acenaphthene	129733	4166.7	0.0321
Acenaphthylene	12269	541.7	0.0441
Anthracene	47707	1708.3	0.0358
Benzo(a)anthracene	26674	400.0	0.0150
Benzo(a)pyrene	21619	45.8	0.0021
Benzo(b)fluoranthene	12696	41.7	0.0033
Benzo(e)pyrene	5641	41.7	0.0074
Benzo(g,h,i)perylene	9313	179.2	0.0192
Benzo(k)fluoranthene	13434	41.7	0.0031
Biphenyl	6367	320.8	0.0504
Chrysene	24357	91.7	0.0038
Dibenzo(a,h)anthracene	5135	41.7	0.0081
Fluoranthene	53194	170.8	0.0032
Fluorene	57275	1208.3	0.0211
Indeno(1,2,3-cd)pyrene	8610	41.7	0.0048
Naphthalene	370582	2208.3	0.0060
Perylene	1435	41.7	0.0290
Phenanthrene	149411	258.3	0.0017
Pyrene	73452	408.3	0.0056
		Geometric Mean:	0.0146

In summary for both benthic invertebrates and fish, the sum of the measured and estimated PAHs and VOCs is the EPC concentration used for the relevant COPC as the dose term to wildlife.

5.2.3.2 Doses for Wildlife from Soil Invertebrates

The bioaccumulation factors for antimony, barium, cadmium, copper, lead, mercury, selenium, thallium, and zinc were taken from Sample et al. (1999) and Efroymson et al. (2001), or for manganese and thallium uptake into plants, from Baes et al. (1984). Bioaccumulation factors for plants, soil invertebrates and wildlife, potentially exposed to PAHs, were taken from U.S. EPA (2005).

5.2.4 Exposure Estimation for Benthic Invertebrates

The EPCs for metals for benthic macroinvertebrates are based upon mean and UCL_{95} concentration of total metals in sediment. Table 5-12 presents UCL_{95} statistics for estimated metal concentrations for COPCs in sediment collected from the Site. A description of the sediment sampling and summary of the sediment data can be found in Appendix B.

Table 5-12. Summary Statistics for Concentrations of Metal COPCs Measured in Site Sediment (mg/kg)

Constituent	Number of Samples	Number of Detections	Concentration (mg/kg)				
			Minimum Detected Concentration	Maximum Detected Concentration	Average Concentration	UCL95 Concentration	95% UCL Method
Barium	72	72	5.3	180	46.83	52.63	Student's-t
Copper	72	72	1.8	700	72.48	91.38	Standard Bootstrap
Selenium	72	21	0.83	16	1.63	1.99	Standard Bootstrap
Thallium	72	14	0.7	4.1	1.47	1.60	Standard Bootstrap

For organics, the EPCs were developed from tissue concentrations measured in the *L. variegatus* bioaccumulation study or estimated based on BSAFs derived from data obtained in the bioaccumulation study as described in Section 5.2.3.1. Estimated benthic invertebrate tissue concentrations used as EPCs in the food chain models are presented in Appendix I, Table I-3.

Measured or estimated concentrations of VOCs and PAHs were also compared to the NEBR developed from the target lipid model in Section 5.1. Body burdens of VOCs and PAHs measured in *L. variegatus* in the 17 samples from the bioaccumulation study are provided in Appendix B, Attachment 2, Table 3.1. Table 5-13 provides summary statistics for the total PAH and VOC concentrations measured during the bioaccumulation study.

Table 5-13. Summary Statistics for Total PAH and VOC[1] Concentrations Measured in *Lumbriculus. variegatus* and Site Fish (µmol/g lipid)

Species	Number of Samples	Total PAH & VOC Concentrations (µmol/g lipid)			
		Minimum Concentration	Maximum Concentration	Average Concentration	UCL95 Concentration
Lumbriculus variegatus	17	0.130	4.08	1.25	1.83
Combined Fish	23	0.008	0.136	0.040	0.051

Notes:

1, VOC concentrations estimated as 3.1% of total PAH concentration measured in *L. variegatus* (See Section 5.1.2.2)
2, 95% UCL = 95% Upper Confidence Limit
3. PAHs = Polycyclic Aromatic Hydrocarbons; VOCs = Volatile Organic Compounds
4, Combined Fish = combined data from bass, bullhead and smelt
5, Both datasets fit a gamma distribution; standard bootstrapping was used to calculate UCL95 concentrations

Estimated benthic invertebrate tissue concentrations calculated based on UCL_{95} sediment concentrations and BSAFs as described in Section 5.2.3.1 are presented in Table 5-14. The total

PAH and VOC concentration estimated in benthic invertebrates (μmol/g lipid) was used as the EPC for Site-wide comparisons to the NEBR.

Table 5-14. Total PAH and VOC Concentrations Estimated in Benthic Invertebrates (µmol/g lipid) Based on Geometric Mean BSAFs and UCL_{95} Sediment Concentrations.

Analyte	Molecular Weight (g/mol)	UCL_{95} Sediment Concentration (mg/kg, dry weight)	UCL_{95} NOC-PAH (mg PAH/kg OC)[a]	Normalized BSAF (kg OC/kg lipid)[b]	Lipid Normalized Molar Concentration (µmol/g lipid)[c]
PAHs					
Total PAHs & VOCs[d]		408.2	2198		47.0
PAHs:					
1-Methylnaphthalene	142.20	5.49	29.55	1.01	0.21
1-Methylphenanthrene	192.26	1.22	6.56	9.31	0.32
2,3,5-Trimethylnaphthalene	170.26	0.56	3.01	6.80	0.12
2,6-Dimethylnaphthalene	156.23	4.13	22.23	2.96	0.42
2-Methylnaphthalene	142.20	85.75	461.79	1.43	4.63
Acenaphthene	154.21	37.62	202.60	1.27	1.67
Acenaphthylene	152.20	3.56	19.16	3.44	0.43
Anthracene	178.20	13.84	74.50	3.02	1.26
Benzo(a)anthracene	228.29	7.74	41.66	6.38	1.16
Benzo(a)pyrene	252.31	6.27	33.76	3.31	0.44
Benzo(b)fluoranthene	252.32	3.68	19.83	5.63	0.44
Benzo(e)pyrene	252.31	1.64	8.81	7.31	0.26
Benzo(g,h,i)perylene	276.34	2.70	14.54	2.71	0.14
Benzo(k)fluoranthene	252.32	3.90	20.98	9.01	0.75
Biphenyl	154.00	1.85	9.94	1.27[e]	0.08
Chrysene	228.29	7.06	38.04	7.32	1.22
Dibenzo(a,h)anthracene	278.35	1.49	8.02	7.69	0.22
Dibenzofuran	168.19	0.30	1.63	1.27[e]	0.01
Fluoranthene	202.26	15.43	83.07	7.18	2.95
Fluorene	166.20	16.61	89.44	2.42	1.30
Indeno(1,2,3-cd)pyrene	276.34	2.50	13.45	1.95	0.09
Naphthalene	128.19	107.47	578.72	3.12	14.10
Perylene	252.31	0.42	2.24	7.01	0.06
Phenanthrene	178.20	43.33	233.33	6.87	8.99
Pyrene	202.26	21.30	114.71	7.45	4.22
Total PAHs[f]		364.02	1960.25		45.52
VOCs:					
Benzene	78.11	0.54	2.91	3.12[g]	0.12
Toluene	92.14	1.57	8.45	3.12[g]	0.29
Ethylbenzene	106.17	2.32	12.52	3.12[g]	0.37
Xylenes (total)	318.50	4.37	23.51	3.12[g]	0.23
m & p-cresols	324.42	0.38	2.02	3.12[g]	0.02
o-cresol	108.14	0.06	0.34	3.12[g]	0.01
1,2,4-Trimethylbenzene	120.20	1.80	9.68	3.12[g]	0.25
1,3,5-Trimethylbenzene	120.20	1.30	7.00	3.12[g]	0.18
Trimethylbenzenes (total)					0.43

Notes:

a, NOC-PAH calculated based on the UCL95 fraction of sediment organic carbon (0.1857) measured in the Site area.

b, Normalized BSAF (kg OC / kg lipid) calculated based on the site-specific 28-day *Lumbriculus variegatus* bioaccumulation study. A normalized BSAF was calculated as the geometric mean of BSAFs for each individual PAH compound (BSAFs were normalized by lipid content [geometric mean of all organisms = 0.0157] and sediment organic carbon content [geometric mean of all samples = 0.1857]).

c, Molar concentration of PAHs in tissue calculated on a mass lipid basis (µmol PAH/g lipid) as follows:

$$C_{tissue} = NOC - PAH \times BSAF_{norm} \div MW$$

where: C_{tissue} = Molar concentration of PAHs in tissue on a mass lipid basis (µmol PAH/g lipid)
NOC-PAH = PAH concentration normalized to organic carbon (mg PAH/kg OC)
$BSAF_{norm}$ = Normalized BSAF (kg OC/kg lipid)
MW = Molecular weight of compound (g/mol)

d, Calculated as the sum of estimated concentrations for listed PAH and VOC compounds.

e, Normalized BSAF for acenaphthene used as a surrogate BSAF for biphenyl based on similar log K_{ow}.

f, Calculated as the sum of estimated concentrations for listed PAH compounds.

g, Normalized BSAF for naphthalene used as a surrogate for VOCs based on the assumption that VOCs are not accumulated at a greater rate than naphthalene (Roubal et al. 1977).

5.2.5 Exposure Estimation for Fish and Pelagic Receptors

There were no COPCs for surface water so no surface water EPCs for fish and pelagic receptors were estimated. Instead, the potential for adverse effects to fish was estimated by comparing the tissue concentrations of fish collected at the Site to NEBRs for fish developed using the target lipid model discussed in Section 5.1. Appendix C summarizes the fish tissue data that was used as the EPC. Table 5-13 presents the UCL_{95} of these data after conversion to μmol/g lipid.

6.1 INTRODUCTION

During Risk Characterization, information developed in the exposure analysis and effects analysis are integrated to estimate the likelihood of adverse effects to the assessment endpoints. Lastly a discussion of the uncertainty associated with each element of the BERA is provided as a context for the conclusions of the Risk Characterization.

The Risk Characterization quantifies potential risks associated with each combination of exposure and effects data. This approach develops risk estimates for receptors inhabiting or utilizing the Site by comparing the estimated EPCs or average dietary doses (ADDs, for birds and mammals) of COPCs (developed in Section 5.2) to a corresponding toxicity reference value or benchmark (Section 5.1). The HQ for each complete exposure pathway, that is, each combination of COPC, ROC, and exposure route, was calculated by dividing the EPC or ADD by the respective TRV or benchmark:

$$HQ = \frac{EPC \ \text{ or } \ ADD}{TRV}$$

The HQ provides an index that expresses the relationship between predicted exposure point concentrations (the EPCs or ADDs) and derived toxicological reference values or benchmarks. If the HQ is greater than one, it indicates that exposure might exceed a known "safe" (no-adverse-effect) concentration for the given receptor, COPC, and exposure pathway and that this particular pathway should be considered in greater depth. A HQ less than one indicates that adverse effects are extremely unlikely because of the inherent conservatism (protectiveness) built into the Exposure and Effects Characterizations, e.g., maximizing exposure potential coupled with protective TRVs or benchmarks.

In some cases in this BERA the HQ is supplemented with other lines of evidence, e.g., evaluation of site-specific toxicity tests and site-specific field surveys, which also provide a perspective on the potential for adverse effects to selected ecological receptors. Thus, for aquatic receptors like benthic invertebrates the results of sediment bioassays and community studies are used as separate lines of evidence to evaluate the potential for adverse effects. As indicated in Section 4.3, the lines of evidence used in this BERA are accorded the following weight of evidence [numbered according to relative significance, with 1) having greater weight than 3)]:

1) Comparison of observed effects in the receptor group community characteristics in waterbodies in and adjacent to the Site to receptor group community characteristics from reference areas;
2) The results of bioassays conducted using standardized toxicity tests with sediments in and adjacent to the Site and surrogate test organisms; and
3) Comparison of Site-specific media concentrations and/or estimated ingested contaminant dose estimates (the latter for wildlife) to effects levels (TRVs and benchmarks) for the various ROCs.

All risk estimates for mammals and birds in the following section are based upon the very conservative assumptions that all chemicals are 100% bioaccessible and bioavailable and that wildlife only feed on prey from the Site area. Obviously these are very conservative assumptions. The details of the calculation of HQs for wildlife are provided in Appendices F and I.

The Risk Characterization is presented by Assessment Endpoint so the results can be easily related back to the Problem Formulation (Section 3.11) and Table 4-1.

6.2 RISK CHARACTERIZATION BY ASSESSMENT ENDPOINT

6.2.1 Assessment Endpoint #1: Viability and Function of Benthic Macroinvertebrate Community

The benthic macroinvertebrate community was selected as an assessment endpoint due to its role in energy flow and materials cycling, its potential for exposure to contaminants, and its role as a food source for higher trophic level organisms.

<u>Risk Question:</u>

Are concentrations of contaminants in the sediments at the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?

This endpoint was assessed using several measurement endpoints as part of four lines of evidence. Three of these lines of evidence make up the Sediment Quality Triad discussed in Section 3.3 and Appendix B.

1) Compare concentrations of metals measured in Site sediment to WDNR (2003) sediment quality guidelines for threshold effects concentration (TEC) and probable effect concentration (PEC).
2) Evaluate the bioavailability of sediment associated divalent metal COPCs using SEM:AVS equilibrium partitioning.
3) Evaluate the affect of soot and coal in the sediment on bioavailability of PAHs using equilibrium partitioning;
4) Compare concentrations of PAHs that accumulated in worm tissues in the bioaccumulation bioassay to the NEBR that is associated with narcosis caused by PAHs and VOCs. Use this as a model for uptake of sediment COPCs by benthic invertebrates at the Site.
5) Determine which sediments at the Site have elevated toxicity to surrogates for resident macroinvertebrate species compared to sediments in reference areas.
6) Determine where benthic communities inhabiting sediments in Site waters are impaired when compared to benthic communities inhabiting reference area sediment.

6.2.1.1 Measurement Endpoint 1): Comparison of Sediment COPCs to Benchmarks for Benthic Infauna

Barium, copper, selenium and thallium had hazard quotients greater than one based upon the WDNR (2003) sediment TEC. No metals exceeded the PEC.

Table 6-1. Hazard Quotients > 1 for Sediments Based upon the UCL_{95} and the TEC.

Metal	Hazard Quotient
Barium	1.1
Copper	2.9
Selenium	2.0
Thallium	2.3

6.2.1.2 Measurement Endpoint 2): Determine Bioavailability of Divalent Metals (Cadmium, Copper, Lead, Nickel and Zinc) Based Upon Equilibrium Partitioning to Acid Volatile Sulfides

Based upon SEM:AVS data copper, the only divalent metal whose HQ exceeded 1, is possibly bioavailable in Site sediments. The SEM:AVS ratio was less than one only at one station, SQT5, where copper exceeded the WDNR screening guidelines (Appendix B: Attachment 1). At the other stations where copper exceeded the WDNR screening guideline, AVS was not detected. These results don't necessarily indicate that the copper is bioavailable because organic carbon which was found at levels of 5 to 50% at Site stations (Appendix B: Attachment 1) can also act as a ligands which further reduces the bioavailability of divalent metals (Besser et al. 2003; Mahoney 1996).

6.2.1.3 Measurement Endpoint 3): Comparison of Benthic Worm Body Burden to No Effects Body Residue

Relative to the NEBR (3.79 μmol/g lipid), individual HQs from the bioaccumulation tests, ranged from 0.03 (SQT2) to 1.08 (SQT5), and the UCL95 of the benthic worm body residues (1.83 μmol/g lipid) resulted in an HQ < 1 (HQ=0.48) (see Appendix B, Attachment 2, Table 3.1).

Extrapolation of the Site-wide sediment PAH concentration to the Site-wide worm body residue (47.0 μmol/g lipid; Table 5-14) resulted in an HQ of 12.4. As explained above this is likely very conservative because it applies a BSAF calculated from much lower concentrations to the much higher Site sediment concentrations.

6.2.1.4 Measurement Endpoint 4): Results of Sediment Toxicity Testing

As discussed in Section 5.1.2.2, sediment toxicity test results indicated that there were significant effects in some bioassays including:

1) Significant mortality at SQT1 and SQT7 in the 28 day test *H. azteca* under laboratory light;

2) Significant mortality at SQT1 and the 50% dilution of SQT1 in the *H. azteca* 10 day test under laboratory light;
3) Mortality to all *L.variegatus* in SQT1 and SQT7 in the bioaccumulation screening test; and
4) The bioassays conducted under UV light indicated effects thresholds at lower concentrations of PAHs.

Derivation of preliminary remediation goals (PRGs) protective of the survival, growth, and reproduction of benthic invertebrate communities is described in the Remedial Action Objectives Technical Memorandum, provided as Appendix A to the RI.

6.2.1.5 Measurement Endpoint 4): Benthic Community Evaluation

Levels of PAHs in Site sediments did not consistently explain any variation in the benthic community, however, grain size and substrate type were significant explanatory factors. For most of the benthic community measures the finer grain sizes were associated with lower values (Appendix B). The overall results suggest that PAH levels (whether TPAH or NOC-PAH) are playing only a minor role in structuring communities, overshadowed by other substrate effects (e.g., grain size and whether the substrate category was wood or sand) (See Appendix B: Attachment 3 for full discussion).

Based upon these results, COPCs in Site sediments are not affecting the benthic community living there.

6.2.1.6 Benthic Community Risk Description

Of the various lines of evidence used to evaluate the benthic community the most weight is accorded to the results of community studies, the least weight is accorded to the comparison of Site COPC levels to effects levels from the literature.

Three lines of evidence, bulk sediment chemistry, sediment toxicity testing and estimated levels of COPCs in benthic invertebrate tissue, indicated a potential of impairment at the community level. This evidence included HQs greater than one for some metals and for PAHs as well as significant effects at some stations to test organisms in the sediment bioassays. The level of COPCs in the bioassay organism, *L. variegatus*, only exceeded the NEBR in two of the bioassay replicates and the HQ based upon the UCL_{95} of the bioassay replicates was less than one. However, the estimated levels of COPCs in site macroinvertebrates which were based upon BSAFs developed from the bioaccumulation study exceeded the NEBR (HQ=12.3).

In contrast, the benthic macroinvertebrate community investigation, the line of evidence that should be accorded the highest weight of evidence because it integrates the effects of contaminants and physical conditions experienced by the Site-specific organisms, indicated that the benthic macroinvertebrate community at the Site was not impaired relative to benthic communities in reference areas.

Considering all lines of evidence leads to the conclusion that elements of the benthic macroinvertebrate community at the Site are probably impacted, however, this impact is not manifested at the community level of organization. This could be due to a variety of factors such as adaptation of the organisms that actually live in Site sediment or selection of species throughout Chequamegon Bay that are tolerant of a wide range of conditions. It could also be explained by the fact that the levels of PAHs in a six inch (15cm) deep sediment sample are not the exposure medium for the majority of the small benthic epifaunal and infaunal species that constitute the benthic community at the Site and in Chequamegon Bay. This is because these benthic organisms are primarily exposed to the top two to three inches. It is likely that the levels of Site chemicals in the top two to three inches is less than a composite sample of the top six inches.[18] If this is the situation, then comparing the levels of PAHs in the top six inches to the results of a grab sample that may have all the benthic organisms in the top two or three inches of the grab effectively separates cause (PAH level) from potential effect (impairment of benthic community).

Lastly, these results could reflect the fact that the species populations that make up benthic communities in Chequamegon Bay are limited by factors other than contaminants in the sediment. Any effects exerted at the individual level, as suggested by the bioassays, are overshadowed by limiting factors such as predation, niche availability (including substrate type and grain size) or food supply. The reproductive potential of these opportunistic benthic species is apparently sufficient to sustain a benthic community throughout Chequamegon Bay that is fairly similar but which may have small scale heterogeneity as the result of substrate characteristics. In this scenario, the levels of contaminants in the sediment would have no more influence on the benthic community than would a non-limiting variable.

Benthos outside the immediate Site area would not be affected by Site-related COPCs since they are not directly exposed to them at levels that would result in impairment too their health.

6.2.2 Assessment Endpoint #2: Viability and Function of Fish Community

The fish community was selected as an assessment endpoint because of its significant role in lake energy flow, nutrient cycling and organic matter accumulation and because fish are an important food resource for higher trophic level species.

[18] Note that the original RI/FS Work Plan recommended sampling only the top four inches (10cm).

Risk Question:

Are concentrations of contaminants in sediments and surface waters of waterbodies in and adjacent to the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?

This endpoint was assessed using three measurement endpoints.

1) Compare concentrations of Site-related contaminants measured in Site surface water to surface water quality benchmarks.
2) Compare tissue levels of PAHs and estimated VOCs in wild fish caught at the Site to the NEBR.
3) Determine where Site sediment has elevated toxicity to surrogates for resident fish species compared to sediment from reference areas.

6.2.2.1 Measurement Endpoint 1): Comparison of Surface Water COPCs to Surface Water Quality Benchmarks

No Site contaminants exceeded screening levels so there were no surface water COPCs.

6.2.2.2 Measurement Endpoint 2): Wild Fish Body Burdens to NEBRs

Comparison of the estimated UCL_{95} of wild fish collected at the Site (0.051 μmol/g lipid) to the NEBR for PAHs (3.79 μmol/g lipid) resulted in an HQ < 1 (HQ = 0.01).

6.2.2.3 Measurement Endpoint 3): Results of Sediment Toxicity Testing using P. promelas

Based upon the results of sediment bioassays there was significantly lower growth at SQT1. There was no mortality of these fish at any of the Triad stations tested in the bioassay under natural light.

Based upon the results of tests from both the 2001 (SEH 2002) and 2005-2006 bioassays with *P. promelas*, a sediment NOEC 40 to 60 μg/g PAHs@1%OC is proposed based upon the endpoints from both the 2001 (SEH 2002) and 2005-2006 bioassays with *P. promelas* (Appendix B: Attachment 2).

The bioassays conducted under UV light indicated effects thresholds at lower concentrations of PAHs.

6.2.2.4 Fish Community Risk Description

Based upon these three lines of evidence it is unlikely that fish utilizing the Site waters are significantly affected by Site COPCs. Although LMW PAHs (and perhaps VOCs) were accumulated to levels above reference conditions, they did not reach levels approaching the NEBR for PAHs. The bioassays using larval fish surrogates for Site fish experienced sublethal effects only at the highest concentrations of PAHs tested. No lethal effects were observed under laboratory light.

Fish outside the immediate Site area would not be affected by Site-related COPCs since they are not directly exposed to them at levels that would result in impairment to their health. Neither should fish outside the Site area be indirectly exposed to PAHs accumulated in fish which fed in the Site area since those accumulated PAHs rapidly be metabolized.

Based upon this evidence it is concluded that the fish community which utilizes the Site waters is within the range of natural variability of fish communities in other habitats in the region and is adequate to provide suitable forage for other indigenous fish and wildlife species.

6.2.3 Assessment Endpoint #3: Viability and Function of Omnivorous Aquatic Bird Community

Omnivorous aquatic birds were selected as an assessment endpoint because they have an important role in energy transfer from the aquatic to the terrestrial ecosystem. Consumers of both aquatic plants and animals, they, in turn, provide an important food source for higher trophic levels.

<u>Risk Question:</u>

Are dietary exposure levels of Site-related COPCs sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?

This endpoint will be assessed using one measurement endpoint.

1) *Through food chain models for the black duck using sediment to benthic invertebrate* bioaccumulation factors, estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.3.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for Omnivorous Aquatic Birds

The estimated dose of total PAHs and VOCs to black duck slightly exceeded the conservative NOAEL (16.1 mg /kg BW/day) resulting in an HQ of 1.9 (Appendix I, Table I-5). Comparison to a NOAEL for total PAHs and VOCs of 161 mg/kg BW/day resulted in an HQ substantially less than one. HQs were less than one for other COPCs based on NOAELs; HQs for all COPCs were less than one based on LOAELs.

6.2.3.2 Omnivorous Aquatic Bird Community Risk Description

It is unlikely that there are any unacceptable impacts to populations of omnivorous aquatic birds. Risk estimates were less than one based upon the NOAEL, with the exception of total PAHs and VOCs, which resulted in an HQ of 1.9 based the conservative NOAEL used at the direction of USEPA. Risk estimates based on an alternative NOAEL endpoint resulted in HQs substantially less than one. Furthermore, since there were no data for the approximately 30% of the black duck's diet that is made up of plants, due to the lack of contaminant data for submerged vegetation or reliable sediment to submerged plant bioaccumulation factors, it was conservatively assumed that the black duck consume 100% invertebrates. Thus, the model food chain for the black duck is conservative.

Based upon this evidence it is concluded that dietary exposure levels of Site-related contaminants are not sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community.

6.2.4 Assessment Endpoint #4: Viability and Function of the Omnivorous Terrestrial Bird Community

Terrestrial omnivorous birds were selected as an assessment endpoint because they consume plant and animal tissue from several different tropic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals.

Risk Question:

Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?

This endpoint will be assessed using one measurement endpoint.

1) Through food chain models for the red-winged blackbird using soil-to-vegetation and soil-to-invertebrate bioaccumulation factors estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.4.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for Omnivorous Birds

The estimated doses of cadmium, zinc, and total PAHs to red-winged blackbird slightly exceeded the NOAEL TRVs (Table 6-2). Comparison of the dose of total PAHs and VOCs to a NOAEL of 161 mg/kg BW/day resulted in an HQ substantially less than one (Appendix I; Table I-6). HQs based on NOAELs were less than one for all other COPCs. Estimated doses of all COPCs were lower than LOAEL doses.

Table 6-2. Risk Estimates for the Red-Winged Blackbird Based upon NOAEL for HQs>1.

COPC	Hazard Quotient
Cadmium	1.1
Zinc	1.2
Total PAHs	1.2[a] / <1[b]

Notes:
a, HQ based on conservative NOAEL of 16.1 mg/kg BW/day
b, HQ based on NOAEL of 161 mg/kg BW/day

6.2.4.2 Omnivorous Bird Community Risk Description

Dietary exposure levels of Site-related COPCs are not sufficient to cause adverse alterations to the omnivorous avian community. The HQ for zinc was based on the minimum (emphasis added) daily requirement of zinc for birds. It is unlikely that a dose slightly exceeding the MDR would exert a toxic effect on the omnivorous bird communities at the Site. The calculated dose of all COPCs also assumed continuous exposure (e.g., area use factor equal to one) of red-winged blackbird to the EPC calculated for the Site. Continuous exposure is unlikely and given HQs that are comparable or less than NOAEL doses, it is unlikely that even continuous exposure would result in adverse effects to the omnivorous bird community. As previously stated, estimated doses were lower than LOAELs for all COPCs. See Section 6.2.10 for a discussion of all terrestrial wildlife.

6.2.5 Assessment Endpoint #5: Viability and Function of the Insectivorous Bird Community

Insectivorous birds were selected as an assessment endpoint because they consume insects and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous avian community?

This endpoint will be assessed using one measurement endpoint.

1) Through food chain models for the tree swallow using sediment to emergent aquatic insect bioaccumulation factors, estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.5.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for Insectivorous Birds

The estimated dose of total PAHs and VOCs to tree swallow exceeded the conservative NOAEL (16.1 mg /kg BW/day) resulting in an HQ of 3.1 (Appendix I, Table I-7). However, comparison to the NOAEL of 161 mg/kg BW/day resulted in an HQ substantially less than one. HQs were less than one for other COPCs based on NOAELs; HQs for all COPCs were less than one based on LOAELs.

6.2.5.2 Insectivorous Bird Community Risk Description

Dietary exposure levels of Site-related COPCs are not sufficient to cause adverse alterations to the insectivorous avian community. The estimated dose of total PAHs and VOCs to tree swallow was substantially lower than the NOAEL dose of 161 mg/kg BW/day. Doses of all other Site-related COPCs did not exceed NOAEL doses. See Section 6.2.11 for a discussion of all aquatic dependent terrestrial wildlife.

6.2.6 Assessment Endpoint #6: Viability and Function of the Piscivorous Bird Community

Piscivorous birds have been selected as an assessment endpoint because they eat primarily fish and thus serve as an important pathway for nutrients and energy from the aquatic to the terrestrial ecosystem. They are also usually the highest trophic level in the food chain and would thus be potentially vulnerable to any contaminants that would bioaccumulate.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations, including reproductive impairment, to the piscivorous avian community or to individual ospreys?

This endpoint will be assessed using two measurement endpoints.

1) Through food chain models for the double-crested cormorant and osprey using actual levels of Site-related COPCs measured in fish, as well as sediment-to-fish bioaccumulation factors estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

Piscivorous birds were considered to forage in aquatic areas. Consumption of contaminated food (100% fish) exposure pathway was evaluated for both species.

6.2.6.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for the Double-Crested Cormorant

No HQ exceeded one for the cormorant (Appendix I; Table 8).

6.2.6.2 Measurement Endpoint 2): Comparison of Modeled Dietary Exposure Doses to Reference Doses for the Osprey

No HQ exceeded one for the osprey (Appendix I; Table 9).

6.2.6.3 Piscivorous Bird Community Risk Description

Dietary exposure levels of Site-related contaminants are not sufficient to cause adverse alterations to the piscivorous avian community. See Section 6.2.11 for a discussion of all aquatic dependent terrestrial wildlife.

6.2.7 Assessment Endpoint #7: Viability and Function of the Omnivorous Mammal Community

Omnivorous mammals were selected as an assessment endpoint because they consume plant and animal tissue from several different tropic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the omnivorous mammal community?

This endpoint will be assessed using two measurement endpoints.

1) Through food chain models for the white-footed mouse using soil-to-plant and soil-to-insect bioaccumulation factors estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.7.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for the White-footed Mouse

The estimated dose of cadmium to white-footed mouse slightly exceeded the NOAEL TRV used at the direction of USEPA (Appendix I; Table I-10). The dose of cadmium to white-footed mouse resulted in an HQ of 1.3 based on the NOAEL and was substantially lower than the LOAEL dose. HQs based on NOAELs were less than one for all other COPCs. Estimated doses of all COPCs were lower than LOAEL doses.

6.2.7.2 Omnivorous Mammal Community Risk Description

Dietary exposure levels of Site-related contaminants are not sufficient to cause adverse alterations to the omnivorous mammal community. The dose of cadmium to white-footed mouse only slightly exceeded the NOAEL dose and was substantially lower than the LOAEL dose. See Section 6.2.10 for a discussion of all terrestrial wildlife.

6.2.8 Assessment Endpoint #8: Viability and Function of the Insectivorous Mammal Community

Insectivorous mammals were selected as an assessment endpoint because they consume insects from several different tropic levels and thus have an important role in energy transfer from plant tissue to animal tissue. They also serve as prey items for higher trophic levels, including both birds and mammals.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations, including reproductive impairment, to big brown bats?

This endpoint will be assessed using one measurement endpoint.

1) Through food chain models for the big brown bat using sediment-to-emergent aquatic insect bioaccumulation factors, estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.8.1 Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for the Big Brown Bat

No HQs for the big brown bat exceeded one.

6.2.8.2 *Insectivorous Mammal Community Risk Description*

Dietary exposure levels of Site-related contaminants are not sufficient to cause adverse alterations to the insectivorous mammal community. See Section 6.2.11 for a discussion of all aquatic dependent terrestrial wildlife.

6.2.9 Assessment Endpoint #9: Viability and Function of the Piscivorous Mammal Community

Piscivorous mammals have been selected as an assessment endpoint because they eat primarily fish and thus serve as an important pathway for nutrients and energy from the aquatic to the terrestrial ecosystem. They are also are the usually the highest trophic level in the food chain and would thus be potentially vulnerable to any contaminants that would bioaccumulates.

Risk Question:

Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?

This endpoint will be assessed using one measurement endpoint.

1) Through food chain models for the mink using actual levels of Site-related COPCs measured in fish, as well as sediment-to-fish bioaccumulation factors, estimate the ingestion of Site-related COPCs and compare it to TRVs associated with adverse effects, including reproductive impairment.

6.2.9.1 *Measurement Endpoint 1): Comparison of Modeled Dietary Exposure Doses to Reference Doses for the Mink*

Piscivorous mammals were considered to forage in the wetland and lentic areas in riparian areas. Consumption of contaminated food (100% fish) exposure pathway was evaluated.

No HQs for the mink exceeded one.

6.2.9.2 *Piscivorous Mammal Community Risk Description*

Dietary exposure levels of Site-related contaminants are not sufficient to cause adverse alterations to the piscivorous mammal community. See Section 6.2.11 for a discussion of all aquatic dependent terrestrial wildlife.

6.2.10 Risk Description for Terrestrial Wildlife

Since HQs only slightly exceeded one (HQs < 1.3) for two terrestrial wildlife ROCs based on NOAEL TRVs, unacceptable alterations at the population or community level to any valued terrestrial receptors under current conditions are unlikely. Since an area use factor of one, meaning that it was assumed all wildlife foraged exclusively on the Site, was assumed even these results are very conservative.

6.2.11 Risk Description for Wildlife Dependent upon Aquatic Prey

Under current conditions, unacceptable alterations at the population or community level are unlikely for any valued wildlife dependent on aquatic prey. HQs only exceeded one (HQs < 3.1) based on a conservative NOAEL used at the direction of USEPA for two wildlife ROCs potentially exposed to total PAHs and VOCs. HQs based on alternative an NOAEL endpoint for total PAHs and VOCs resulted in HQs substantially less than one for all wildlife dependent on aquatic prey. Since the HQ for the osprey did not exceed one either, individual ospreys would not be unacceptably affected. Since an area use factor of one, meaning that it was assumed all wildlife forged exclusively on the Site, was assumed even these results are very conservative.

6.2.12 Terrestrial Ecosystem Functionality

The upland area of the Site is either urban or utilized for recreational purposes without regard to terrestrial receptors. Due to the virtual absence of any natural habitat in the upland area, it is unlikely that the area supports any populations of valued ecological receptors.

6.2.13 Aquatic Ecosystem Functionality

While there have been no Site-specific direct measurements of the functionality of aquatic ecosystem, the evaluation of the benthic invertebrate, fish and aquatic wildlife receptor communities can provide an indirect measure of the potential for adverse effects to the aquatic ecosystem. These receptor groups are trophically and ecologically diverse and play a role in various aquatic ecosystem functions including nutrient cycling, energy flow, food production, etc.

Based upon the lines of evidence used in this risk assessment it was concluded that elements of the benthic macroinvertebrate community are potentially impaired in a portion of the Site area due to elevated levels of Site-related contaminants. This following evidence supports this conclusion:

1) Levels of Site-related PAHs and VOCs exceed WDNR benchmarks for sediment quality.
2) Levels of PAHs associated with unacceptable impacts to *H. azteca* in sediment bioassays were in the range of 45 to 100 μg/g @1%OC. Some of the near shore surface sediments exceed that concentration.
3) There was significant mortality at SQT1 and SQT7 in the *H. azteca* 28 day bioassay conducted under laboratory light;
4) There was significant mortality at SQT1 and the 50% dilution of SQT1 in the 10 day test conducted under laboratory light; and
5) There was mortality to all *L.variegatus* in SQT1 and SQT7 in the bioaccumulation screening test.
6) HQs for benthic invertebrates based upon tissue residues estimated from laboratory BSAFs and the UCL Site sediment concentrations exceeded one (HQ=12.3).

However it does not appear, based upon the lines of evidence used in this risk assessment, that populations or communities of other aquatic receptors, have experienced adverse alterations. This conclusion is supported by the following evidence from the BERA:

1) Levels of Site contaminants in fish tissue collected in the immediate Site area were below the NEBR.
2) Only the HQ for zinc slightly exceeded one for aquatic omnivorous birds.
3) HQs for aquatic dependent wildlife, including the tree swallow, big brown bat, double crested cormorant, osprey and mink who potentially feed on emergent aquatic insects or fish from Site waters were below one.

6.2.14 Potential for Adverse Effects to Ecological Receptors from Releases of Contaminants from Subsurface Sediments

Levels of Site-related hydrocarbons in subsurface sediments are sufficiently elevated in some near shore Site sediments that surface sheens occur following some high energy meteorological events or when sediments are otherwise physically disturbed. Regulators and local residents, as well as contractors who have sampled sediments at the Site have observed these sheens. The potential for these releases is primarily in shallower areas where sediments and wood mulch underlying surface sediments are apparently saturated with hydrocarbons. This results in a release of a sheen when the sediments are disturbed.

However, release of substantial quantities of these hydrocarbons is very unlikely. These sheens are typically the lighter fraction of Site hydrocarbons, i.e. short chain alkanes, VOCs and perhaps some LMW PAHs. Since HMW PAHs are too insoluble and/or are crystalline in nature they are probably not part of the sheens that are seen. While sheens are visually obvious the concentrations of the hydrocarbons in a sheen are not necessarily high. It only takes a concentration above the saturation level of these hydrocarbons to result in the free phase. As an example, a silvery sheen results from hydrocarbons when they are about 1/900,000 to 1/200,000 of an inch thick on the water, iridescence ranges from about 1/100,000 to 1/60,000 of an inch thick, dull iridescence with brown streaks about 50,000 to 10,000 inches thick (Wilkinson 1972). The following table (Table 6-3) is a rough guide to the relationship between the color of sheens and the estimated concentration of hydrocarbons.

Table 6-3. Relationship Between Sheen Color and Hydrocarbon Concentration.[1]

Appearance of Oil on Water	Concentrations in ppm
Barely visible	0.05
Silver sheen	0.1
First trace of color	0.2
Bright bands of color, iridescent	0.4
Colors tending to be dull	1.2

Table 6-3. Relationship Between Sheen Color and Hydrocarbon Concentration.[1]	
Appearance of Oil on Water	**Concentrations in ppm**
Colors fairly dark, rainbow tints	2.4
Brown or black	12
Brown / dark brown	120

1: After "Oil Spill Response in the Marine Environment" (Doerffer 1992)

In addition to surface sheens emanating from disturbed sediment, sediment samples collected in some areas of the Site, primarily in areas with the greatest PAH and VOC concentrations in sediment have a chemical odor indicating presence of hydrocarbons. However, the fact that the sediment has an odor does not necessarily imply there are significant levels of hydrocarbons in the sample. For instance the threshold level of commercial gasoline in water is around 5 µg/L with 10 µg/L giving a strong odor. The threshold odor concentration of commercial diesel in water is commonly accepted to be 100 ppb (SWRCB 1963).

Sediments that had this odor during the sediment sampling conducted as part of the RI studies had levels of hydrocarbons in the range of 10's to 100's of µg/g total PAHs plus VOCs. For instance, the sediments at several replicate sediment samples from SQT1 had a hydrocarbon odor and the highest concentration of PAHs was 1162 µg/g (average of all five replicates was about 440 µg/g). Total VOCs in the highest replicate from this SQT1 was about 3.5 µg/g (Appendix B: Attachment A).

Even hydrocarbons at the levels found in sediments at SQT1 would be rapidly diluted in the water column were they to be released from the sediments by waves or by a disturbance. As documented in the surface water investigation conducted as part of these RI/FS studies hydrocarbons were virtually undetectable in surface water, even following high energy events.

Since there are not continual releases to the water column, as evidenced by the absence of sheens at all times and the absence of hydrocarbons in the water column, it is unlikely that pelagic receptors such as fish are directly exposed to harmful levels of Site COPCs and more likely that they acquire their body burden of PAHs through the food chain.

With the exception of major storms or disturbance in the shallow near shore zones by propeller wash or anchors, activities that are presently prohibited, releases of a sufficient quantity of hydrocarbons to acutely affect ecological receptors other than, perhaps, benthos that are on the bottom in the immediate area of the release are unlikely.

Although it is unlikely that sporadic releases of low levels of hydrocarbons from Site sediments will lead to impairment of populations and communities of ecological receptors inhabiting the waters of Chequamegon Bay, it remains a source of uncertainty. It is possible that the presence of this continuing source of site related contaminants may sporadically impair the healthy functioning of the aquatic community in the Site area.

In addition, if normal lake front activities, i.e, wading, boating etc., were not presently prohibited, the disturbance of sediments and concomitant release of subsurface COPCS would increase. This potentially could lead to greater impacts than were measured during these RI studies.

6.3 UNCERTAINTY ANALYSIS

Uncertainties associated with any risk assessment have a number of components, including degree of success in meeting objectives, the range of conditions over which conclusions can be applied, and the certainty with which conclusions can be drawn (USEPA 1989a). The conclusions of a risk assessment are useful only when placed in perspective relative to the uncertainties associated with the evaluation. The purpose of this section is to provide that perspective.

6.3.1 Components of Uncertainty

Uncertainty in risk estimation has both qualitative and quantitative components. Qualitative uncertainty analyses are recommended by guidance, and contribute to the confidence with which risk assessment conclusions can be drawn and applied (USEPA 1989a; 1992a).

Uncertainty has two primary components: absence of knowledge and variability. Absence of knowledge of the quantity of sediment ingested by avian receptor which contributes to its ingested dose of COPCs is an example of the former. Variability refers to observed differences attributable to heterogeneity or diversity in a population or exposure parameter. A difference in COPC concentrations at different locations within a small area is an example of variability.

Variability in a risk estimate has a number of components, including parameter variability, calculation error and simplification, and the underlying reality of exposure assumptions and pathways (USEPA 1989b). It is important to understand that variability includes both real variation (reflecting actual, mechanistic biological response ranges and variability in ecosystem conditions) and error. Thus, because biological systems are inherently uncertain and variable, some component of variability in risk estimation is due to a realistic reflection of ecological conditions, while another component is due to "error" or uncertainty introduced by the overall analytical process. "Error" is the component that can be minimized by additional information and knowledge, because this encompasses uncertainty that has been introduced by the assessment process. However, it is important to understand ecosystem variability because this represents an important component of the ecosystem within which risk management decisions must be made.

6.3.2 General Sources of Uncertainty

Uncertainties surrounding estimates of ecological risk are intrinsically greater than those associated with human health risk assessment, due to the multiplicity of potential receptor species, a general lack of knowledge regarding their life histories and behaviors (particularly with respect to utilization of the Site itself), and the unknowns of toxicological sensitivities among the receptor species. The toxicity benchmarks used in this assessment are intended to provide accurate benchmarks for judging potential exposures, but it is important to note that no one approach to benchmarks derivation is adequate for all sites and chemicals. The best methods currently available were used to evaluate the potential additive effects of the organic chemicals associated with the Site, but potential interactions between inorganic and organic chemicals is only based upon the results of the sediment bioassays that were performed. It is believed that these bioassays fully account for site-specific conditions that regulate chemical contact and bioavailability of these chemicals, but the disturbance and handling of the sediments undoubtedly results in greater exposure than occurs in undisturbed sediments. However, laboratory bioassays cannot reproduce any long-term flux from deep sediments to the biotic zone where benthic organisms live, or the significant influence of other factors resulting from historical use of the Site, such as log rafting and disposal of wood waste.

A qualitative description of many of the uncertainty and variability factors associated with the parameters used to estimate risks to ROCs in this risk assessment are provided in Table 6-4. These factors are generally applicable to both aquatic and terrestrial ecological risk assessments.

Table 6-4. General Factors Associated with Uncertainty and Variability in the Ecological Risk Assessment.		
Uncertainty/Variability Factor	**Direction of Uncertainty**	**Comment**
Use of conservative exposure point concentrations and doses	Will overestimate risk	The intent of using UCL_{95} exposure and dose concentrations is to be protective of biota and minimize effects of uncertainties that underestimate risks.
Point estimates of exposure concentrations of COPCs in environmental media	Tends to overestimate risks	Point estimates do not take into account bioavailability of chemicals or the likelihood of variable exposure concentrations resulting from highly variable spatial heterogeneity of sediment conditions.
Unavailability of toxicity benchmarks and reference values for some chemicals and exposure pathways	Will underestimate risk	Some site risks may be unquantifiable due to lack of TRVs or benchmarks.
Focus of risk assessment on chemicals analyzed and detected	Will underestimate risk	Chemicals not detected or not analyzed for may contribute to risks.
Extrapolation of laboratory data to field exposures	Generally overestimates risk	Receptors adapted to site conditions are likely not as sensitive as laboratory organisms.
Hazard Quotient calculation	May overestimate or underestimate risks	Direction of effect depends on accuracy with which TRVs or benchmarks describe the response of biota to chemicals.
Biota sampling locations	May overestimate or underestimate risks	Locations may not be representative of sites with either extremely elevated or low chemical concentrations.
Use of NOAELs as TRVs when possible instead of LOAELs	Will overestimate risks for most species. May underestimate risks for sensitive species.	The NOAEL is not associated with any effects and is often dependent on range of concentrations tested in laboratory studies. The highest true NOAEL may be higher than NOAEL used as a TRV.

Table 6-4. General Factors Associated with Uncertainty and Variability in the Ecological Risk Assessment.		
Uncertainty/Variability Factor	**Direction of Uncertainty**	**Comment**
Use of LOAEL-based TRVs	May underestimate risks for sensitive species; probably does not markedly overestimate risk for most individuals; uncertain for population-level effects.	LOAELs are more reliable than NOAELs and provide an indication of the dose–response function to aid in interpreting quotients.
Analytical chemistry variability	May overestimate or underestimate risks	Chemical analyses within 35% relative percent difference of each other may be equivalent.

Because the complexity of community and population dynamics, it is not currently possible to evaluate all possible exposures or effects. The information presented, while as complete and accurate as possible, may have missed long-term influences to the environmental chemistry of contaminants found at the Site. It also may have failed to address adaptation of natural communities to the unique site conditions. In addition, while ecological functional redundancies contributed by unevaluated species may provide resiliency against adverse effects at the community and ecosystem levels, more sensitive species may be present in other populations that have not been evaluated in the current studies. In either case, the studies presented are only representations of conditions as they exist at the Site, and it is virtually certain that not all of the underlying variability and stressor effects have been quantified. Therefore, it is important to recognize that (1) potentially large uncertainties exist regarding community and population health, but (2) these uncertainties most probably do not directionally bias conclusions.

Further, it is important to recognize that substantial differences exist between observations and conclusions made at the individual, population, and community levels of biological organization. For example, effects at the population or community levels resulting from the effects to only a few individuals may not be observable with the type of studies implemented. The ramifications of this also include an understanding that because the assessment level endpoints are protective of populations (not individuals), risks projected to cause loss of a few individuals, for example in bioassay studies, may not cause impacts that are important at the levels of assessment where risk management decisions are made, i.e. populations and communities.

The analysis performed for this assessment did not account for some Site-specific factors such as natural attenuation of COPCs over time, adaptive tolerance, adaptive reproductive potential, the small size of the affected area compared to the range of most species, and recruitment from similar adjoining areas, although many of these factors were implicit through measurement of the benthic macroinvertebrate communities. Such factors would tend to mitigate the degree and ecological significance of loss or impairment of a portion of ecological population(s) due to both chemical and physical stressors in the area. As a result, the approach used in this assessment likely results in overestimation of risk.

6.3.3 Specific Sources of Uncertainty

Potential sources of uncertainty in this BERA are discussed in this section and summarized in Table 6-5.

Table 6-5. Specific Factors Associated with Uncertainty and Variability in the Ashland/Lakefront Baseline Ecological Risk Assessment.

Uncertainty/Variability Factor	Direction of Uncertainty	Comment
Adequate sampling	May overestimate or underestimate risks	Sampling is considered to be representative and adequate. It is unlikely any consistent bias exists. The RI Sampling plan was reviewed and approved by USEPA and WDNR and also reviewed by NOAA.
Choice of Receptors of Concern	May overestimate or underestimate risks	Both the number of and the type of ROCs are considered to adequate and representative. It is unlikely any consistent bias exists.
Use of surrogate species toxicological studies as the basis for benchmarks and TRVs	May overestimate or underestimate risks	Care was taken to select studies of the same or closely related species under the same conditions. It is unlikely there is any directional bias in these results.
Relative bioavailability not considered in derivation of wildlife TRVs	Will overestimate risks	Overestimation may be substantial.
Use of laboratory bioassays as the basis for bird and mammal TRVs	Will overestimate risk	Effects levels estimated from field data usually higher than those estimated in the laboratory. Homogenization of sediments results in previously unavailable contaminants becoming available. Exposures to UV light in the lab cannot duplicate natural UV exposure.
Site specific sediment bioassays	Generally overestimates risk	Receptors adapted to site conditions are likely not as sensitive as laboratory organisms. Disturbing sediment changes equilibrium.
Incremental effects of UV Light on benthic organisms and fish	Generally overestimates risks	While the effects of UV light on aquatic organisms have been demonstrated in the laboratory, there are a number factors, including time and space varying transparency of the

Table 6-5. Specific Factors Associated with Uncertainty and Variability in the Ashland/Lakefront Baseline Ecological Risk Assessment.

Uncertainty/Variability Factor	Direction of Uncertainty	Comment
		water column and behavioral adaptations of organisms in the field to avoid UV light that can not be faithfully replicated in the laboratory.
Site specific community studies	May overestimate or underestimate risks	The high natural variability in populations and communities decreases confidence in attributing differences in community structure to only sediment contaminant levels. This uncertainty was addressed by rigorous sampling design and it is unlikely there is any directional bias in these results.
Using area use factor of one	Overestimates risk	An assumption of an area use factor of one assumes that wildlife forage exclusively in the impacted Site areas. However, the majority of receptors used as representative receptors in this risk assessment are mobile and have foraging ranges that exceed areas of the Site with elevated levels of contaminants.
Simplifying wildlife assumptions for diets	May overestimate or underestimate risks	Natural diets are much more complex than those assumed in wildlife models.
Use of bioaccumulation factors for metals in wildlife models	Likely overestimates risk	Much of the data used to develop bioaccumulation factors comes from laboratory studies which are limited with respect to modeling the site-specific bioavailability of contaminants.

6.3.3.1 Uncertainty Associated with Problem Formulation

The Problem Formulation outlines an approach for assessing risk to ecological receptors from exposure to surface water, sediment, and soil within and adjacent to the Ashland Lakefront Site. This approach follows USEPA guidance and was conducted with recommendations from both state and federal stakeholders, including USEPA, NOAA, and WDNR. Both USEPA and WDNR approved the scope of work upon which this BERA is based. The Problem Formulation was developed based on information obtained from various studies that have been conducted at the Site, both historical as well as these RI studies that were designed specifically to support the BERA. These studies decrease the uncertainty of the BERA conclusions by incorporating Site-specific information into the risk assessment process. However, some level of uncertainty remains inherent in the risk assessment process.

Data Quality and Representativeness

Insufficient sampling density or analyte lists may result in misrepresenting estimates of exposure to COPCs. Misrepresentation of exposure results in uncertainty and may lead to an overestimation or underestimation of risk. Additional data collection based on the data gap analysis as part of the RI Work Plan has substantially reduced this uncertainty. The surface water, sediment, fish tissue, benthic community data available for the Site and surrounding areas is considered to be sufficient to support the BERA. However, it is important to recognize that sampling was biased towards impacted areas and away from ambient background conditions.

Receptors of Concern

Because it is not feasible to evaluate every potential ecological receptor that may be exposed to contaminants in Site media, receptor groups and individuals that were believed to typify trophic categories were selected for evaluation. It is assumed that these ROCs are representative of the receptors on the Site that have ecological or societal value. There is some uncertainty associated with whether all ecological values present at the Site and surrounding areas will be adequately represented in the BERA. However, conducting aquatic and terrestrial habitat characterizations of the Site and communicating with relevant state and federal agencies responsible for the protection of ecological resources at the Site have reduced this uncertainty.

The Problem Formulation was developed based on the current knowledge of the ecological resources of the Site and exposure pathways from Site-related media to those ecological resources. It was developed with the frequent review and input of various federal and state regulatory and resource agencies including USEPA, WDNR and NOAA. Despite uncertainties inherent in the risk assessment process, the Problem Formulation outlines an appropriate approach to conducting the BERA agreed upon by all agency stakeholders.

6.3.3.2 Uncertainty Associated with Effects Analysis

Surrogate Species

Organisms used in the toxicological studies from which TRVs and benchmarks were derived were seldom the same species as those used in this risk assessment to estimate risk. To the extent the laboratory species are more or less sensitive then those used as ROCs in this risk assessment, the potential for adverse effects is under or over estimated.

Use of Laboratory Bioassays as the Basis for Bird and Mammal TRVs

The risk to bird and mammal populations may be overestimated if the results of laboratory bioassays are used as a proxy for what happens in the field. This is particularly true of the essential micronutrients, which are homeostatically regulated such as copper, selenium and zinc.

Relative Bioavailability

Relative bioavailability is the ratio of the absorption of a chemical from a site medium compared to the absorption that occurred in the study used to derive the relevant TRV. As a result of this factor, it is likely that exposure, and therefore, risk was over-predicted to all receptors. While there is relative bioavailability data for mammals and birds exposed to some metals these are minor constituents at the Site and 100% bioavailability was assumed for both mammals and birds. Furthermore, there is no mammalian or avian data concerning the bioavailability of PAHs that are biologically incorporated into the diet (i.e., fish). Therefore, 100% bioavailability of PAHs was assumed. Bioavailability data of PAHs in soil, suggest that this assumption is conservative.

Probable Effects on Risk Evaluation of Not Compensating for Bioavailability, Bioaccessibility and Homeostasis

The toxicity tests upon which the avian and mammalian TRVs are based were conducted with COPCs or hydrocarbon mixtures that were added to the diets. Such amended diets may be representative of the exposures wildlife would have through the incidental ingestion of soil or sediment, but this exposure pathway is relatively small portion of the total exposure. For wildlife, the diet is the major portion of the total exposure and the composition of PAHs incorporated into the diet is likely very different from that in the PAH mixture in the environment. This is due to both solubility limitations in the abiotic media (i.e., surface water, or sediment pore water) and metabolism by the food chain items in the diet as well as in the intestine of the final receptor, prior to uptake into the animal. As a result, the doses to the wildlife receptors are likely overestimated.

Uncertainty Associated with Benthic Invertebrate Lines of Evidence

Site-specific Bioassays

Sediment bioassays were conducted as part of the aquatic studies used to assess risk to Site benthic macroinvertebrates. The results of these studies are used to supplement the risk estimates developed from comparing EPCs to benchmarks that may be associated with effects to aquatic organisms. However, these bioassays are imperfect abstractions of real life and may under or overestimate risk.

There are several sources of uncertainty in the bioassay studies including uncertainties associated with:

1) Bioassay duration;
2) Exposure of laboratory organisms to UV light; and
3) Failure of *C. dilutus* bioassay.

Specific details of these uncertainties are discussed in the bioassay report (Attachment 2 to Appendix B).

Because organisms used in the laboratory bioassays are likely to be more sensitive than adapted populations of organisms living at the Site the results of bioassays are likely to overestimate risk.

Since the objective of an ecological risk assessment is to assess the potential impact to biotic populations and communities (except for protected species), it is likely that the results of tests using a few individual organisms in an artificial environment will overestimate the potential for adverse effects to the population. A bioassay does not replicate either the environmental heterogeneity present on the Site or duplicate the population dynamics, including compensatory mechanisms of the population. It also is important to note that nearly all organisms tested have shown the ability to increase their metabolism of PAHs in response to exposure, and that, under natural conditions, natural selection for tolerant organisms is operable. This natural selection does not occur in animals that are bred for bioassays and in fact, these organisms are isolated from nearly all natural stressors that would normally select for more robust organisms.

In summary it is likely that the results of the sediment bioassay overestimated risk to populations and communities of benthic macroinvertebrates.

Site-specific Bioaccumulation Study

Biota-sediment accumulation factors for benthic invertebrates were developed from the laboratory study using *L. variegatus*. The geometric means of BSAFs developed for individual PAHs from the bioaccumulation study were applied to Site-specific sediment concentrations to estimate the concentrations of PAHs in Site benthic invertebrates. Based upon these estimates, estimated tissue residues of PAHs in benthic invertebrate tissues resulted in an HQ greater than one (12.4). At the request of USEPA, concentrations in Site benthic invertebrates were estimated based on the UCL_{95} of BSAFs developed from the bioaccumulation study. Based on the UCL_{95} BSAFs, the estimated concentration of tPAH in benthic invertebrates was 176.6 μmol/g lipid, resulting in an HQ of 46.5 when compared with the NEBR of 3.79 μmol/g lipid (Table 6-6).

The laboratory-generated BSAFs from the *L. variegatus* study are several times greater than what has been measured in field studies or what is theoretically possible based upon the target lipid model (Di Toro et al. 2000). The BSAFs obtained with *L. variegatus* in the bioaccumulation study are site-specific only in that they were obtained using Site sediments. The bioavailability of PAHs in the *L. variegatus* bioaccumulation test is at least partly an artifact of the USEPA test procedures. When samples are composited for bioaccumulation tests (and bioassays) from the top 6 inches of site sediment, higher concentrations from deeper sediment depths are mixed with lower concentrations from the surface layers where most organisms live. This is important because Harkey et al. (1995) also showed that "uptake rate is primarily driven by the first few sampling points [i.e., first few days] during a bioaccumulation assay". This means that, until the overlying surface waters leach the PAHs from the surface layers, bioassay and bioaccumulation organisms are exposed to much higher concentrations than they would be in the field.

Higher bioaccumulation also occurs during tests with <u>*L. variegatus*</u> because they are not being fed for 28-d and lose weight and lipid content. However, lipid content is not necessarily lost in the same proportion as total weight. The worms analyzed at the beginning of the bioassay contained an average of 2.44% lipid and this decreased to 0.5% at one station and less than 2% at most stations

Table 6-6. Total PAH and VOC Concentrations Estimated in Benthic Invertebrates (µmol/g lipid) Based on UCL_{95} BSAFs and UCL_{95} Sediment Concentrations

Analyte	Molecular Weight (g/mol)	UCL_{95} Sediment Concentration (mg/kg, dry weight)	UCL_{95} NOC-PAH (mg PAH/kg OC)[a]	Normalized BSAF (kg 0C/kg lipid)[b]	Lipid Normalized Molar Concentration (µmol/g lipid)[c]
PAHs					
Total PAHs & VOCs[d]		408.2	2198		176.6
PAHs:					
1-Methylnaphthalene	142.20	5.49	29.55	4.09	0.850
1-Methylphenanthrene	192.26	1.22	6.56	38.20	1.30
2,3,5-Trimethylnaphthalene	170.26	0.56	3.01	18.23	0.32
2,6-Dimethylnaphthalene	156.23	4.13	22.23	8.33	1.19
2-Methylnaphthalene	142.20	85.75	461.79	5.72	18.58
Acenaphthene	154.21	37.62	202.60	4.37	5.74
Acenaphthylene	152.20	3.56	19.16	10.49	1.32
Anthracene	178.20	13.84	74.50	10.29	4.30
Benzo(a)anthracene	228.29	7.74	41.66	23.07	4.21
Benzo(a)pyrene	252.31	6.27	33.76	12.15	1.63
Benzo(b)fluoranthene	252.32	3.68	19.83	23.18	1.82
Benzo(e)pyrene	252.31	1.64	8.81	24.59	0.86
Benzo(g,h,i)perylene	276.34	2.70	14.54	8.45	0.44
Benzo(k)fluoranthene	252.32	3.90	20.98	27.62	2.30
Biphenyl	154.00	1.85	9.94	4.37[e]	0.28
Chrysene	228.29	7.06	38.04	25.52	4.25
Dibenzo(a,h)anthracene	278.35	1.49	8.02	22.15	0.64
Dibenzofuran	168.19	0.30	1.63	4.37[e]	0.04
Fluoranthene	202.26	15.43	83.07	28.08	11.53
Fluorene	166.20	16.61	89.44	7.95	4.28
Indeno(1,2,3-cd)pyrene	276.34	2.50	13.45	6.69	0.33
Naphthalene	128.19	107.47	578.72	12.51	56.48
Perylene	252.31	0.42	2.24	12.49	0.11
Phenanthrene	178.20	43.33	233.33	20.42	26.74
Pyrene	202.26	21.30	114.71	37.31	21.16
Total PAHs[f]		364.02	1960.25		170.69
VOCs:					
Benzene	78.11	0.54	2.91	12.51[g]	0.47
Toluene	92.14	1.57	8.45	12.51[g]	1.15
Ethylbenzene	106.17	2.32	12.52	12.51[g]	1.47
Xylenes (total)	318.50	4.37	23.51	12.51[g]	0.92
m & p-cresols	324.42	0.38	2.02	12.51[g]	0.08
o-cresol	108.14	0.06	0.34	12.51[g]	0.04
1,2,4-Trimethylbenzene	120.2	1.80	9.68	12.51[g]	1.01
1,3,5-Trimethylbenzene	120.2	1.30	7.00	12.51[g]	0.73
Trimethylbenzenes (total)					1.74

Notes:

a, NOC-PAH calculated based on the UCL95 fraction of sediment organic carbon (0.1857) measured in the Site area.

b, Normalized BSAF (kg OC / kg lipid) calculated based on the site-specific 28-day *Lumbriculus variegatus* bioaccumulation study. A normalized BSAF was calculated as the UCL_{95} BSAFs for each individual PAH compound (BSAFs were normalized by lipid content [geometric mean of all organisms = 0.0157] and sediment organic carbon content [geometric mean of all samples = 0.1857]).

c, Molar concentration of PAHs in tissue calculated on a mass lipid basis (µmol PAH/g lipid) as follows:

$$C_{tissue} = NOC - PAH \times BSAF_{norm} \div MW$$

where: C_{tissue} = Molar concentration of PAHs in tissue on a mass lipid basis (µmol PAH/g lipid)
NOC-PAH = PAH concentration normalized to organic carbon (mg PAH/kg OC)
$BSAF_{norm}$ = Normalized BSAF (kg OC/kg lipid)
MW = Molecular weight of compound (g/mol)

d, Calculated as the sum of estimated concentrations for listed PAH and VOC compounds.

e, Normalized BSAF for acenaphthene used as a surrogate BSAF for biphenyl based on similar log K_{ow}.

f, Calculated as the sum of estimated concentrations for listed PAH compounds.

g, Normalized BSAF for naphthalene used as a surrogate for VOCs based on the assumption that VOCs are not accumulated at a greater rate than naphthalene (Roubal et al. 1977).

after 28-d. This alone causes an apparent increase in body residue although the relative concentration of PAHs in the lipid may not have changed.

Another possibility for the extraordinarily high bioaccumulation found in these worms is that the depuration period may have been insufficient for them to clear their gut contents. Harkey et al. (1995) report that only 2% of the body residue is released from worms during the 24-h depuration period. If the worms were narcotized, the active portion of depuration would presumably take even longer.

In summary the BSAFs calculated from the *L. variegatus* bioaccumulation study are greater than those typically observed in field studies, as reported in the literature (See Section 5.2.3). We believe therefore that estimates based on the geometric mean BSAFs from the bioaccumulation study provide a conservative estimate of tPAH concentrations in benthic invertebrate tissues for use in wildlife exposure models and direct comparisons with the NEBR. Given the already conservative nature of the BSAFs used in the BERA, calculating tissue concentrations based on the UCL_{95} of BSAFs introduces an additional level of uncertainty that likely overestimates risk.

Site-specific Benthic Macroinvertebrate Community Studies

Because the benchmarks used to evaluate ecological risk, except for protected species, are ultimately impacts to populations and communities of ecological receptors, field studies of natural populations and communities can therefore be the best line of evidence to evaluate impacts from contaminants at the Site. However, because of the inherent natural variability in populations and communities, unless there is a rigorous sampling design, it is difficult to attribute differences amongst Site stations and reference stations to the effects of Site contaminants and conversely to have confidence that the absence of a measured difference is indicative that Site contaminants are not having an effect.

As was explained in the RI/FS Work Plan (URS 2005), care was taken in benthic community studies conducted to support this BERA to get adequate replication of samples so that any differences amongst stations can be considered real and not just random variability. This sampling design included power analysis to ensure that levels of differences that were expected in the benthic community study could be differentiated with reasonable statistical confidence from random variation. However, there is uncertainty associated with the reference locations that produces questionable results and yields low power, including, but not limited to:

- The reference sand sites SQT10 and SQT12 exhibited "a strong odor of decaying organic matter" and "elevated levels of ammonia";

- The reference sand sites SQT10 and SQT12 exhibited <50% survival for *Hyalella azteca* 28 day sediment exposure toxicity test;

- The reference wood site SQT11 had no survival in several replicates of the *Lumbriculus* bioaccumulation study;

- The reference sand sites SQT13 and SQT 14 were collected in Fall 2005 versus Spring 2005, more than 3 months after the initial sample collection. Use of this data is questionable for comparison of population metrics due to expected seasonal variation in larval and emergent species; and

- Only three site locations appear to be "sand" sites, and none of the reference sand sites appear to be appropriate. Thus, the sample size for sand sediments does not appear meet the power requirements outlined in the RI/FS workplan

Uncertainty Associated with Fish Community Lines of Evidence

The results of Site-specific studies are believed to more accurately represent the potential for adverse effects to receptors inhabiting or utilizing the site and thus should be weighted higher than screening guideline values. However, neither the screening values nor the target Lipid Model indicated any risk to the fish community. While there was some mortality of juvenile fathead minnows in tests in 2001, no mortality was found in 2005-2006 bioassays. Furthermore, in both cases the fish were exposed predominately to highly contaminated sediments that had been mixed and as a result water column concentrations in the bioassay likely exceeded conditions in the field. It is likely therefore that bioassays conducted in the laboratory overestimate risk at the Site.

6.3.3.3 Uncertainty Associated with Exposure Analysis

The analytical database used to develop estimates of EPCs has inherent uncertainties. These include those uncertainties associated with spatial allocation of samples, laboratory error and statistical error. For example, because the primary objective of the sampling and analysis plan was to document the magnitude and extent of Site contaminants, sampling was generally concentrated in areas anticipated to have elevated concentrations. As a result estimates of exposure to contaminants for mobile ecological receptors are biased high. Also, the distribution of COPCs across aquatic and terrestrial portions of the site was assumed to coincide with receptor contact with environmental media. The degree to which this assumption is met is not quantifiable and the direction of bias (if any) cannot be identified.

Error due to lack of precision and inaccuracies in the laboratory is believed to be low since controls were in place to identify and quantify precision and accuracy. Likewise any inaccuracy in compiling summary statistics is believed to be low because of controls on the process. Both of these potential sources of error are without bias.

Area Use Factor

The receptors used as ROCs in this BERA are mobile and range beyond the boundaries of the Site while foraging or for other purposes, on a daily or seasonal basis. This risk assessment has assumed that all receptors have an area use factor of 100 percent, which means that they are continually exposed to maximum or upper estimates of the mean (UCL_{95}) COPC levels. This is a deterministic approach to estimating EPCs and is expected to bias the estimates of EPCs upwards and result in an overestimate of risk to most receptors. This assumption also means that each receptor acquires 100% of its diet from the Site area. This assumption is very conservative, thus the estimates of risk based on these assumptions are useful for developing adequately protective remedial actions but cannot be considered as evidence of adverse effects.

There are available risk assessment methodologies such as estimating spatially weighted EPCs or conducting probabilistic modeling of exposure that could be employed to decrease the uncertainty and overestimation of potential risk. However, since HQs for wildlife were not above one, these approaches were not used.

Simplifying Assumptions for Wildlife Diets

In the wildlife dose rate modeling, simplifying assumptions were made about the diet of most wildlife species. It was assumed that all components within a particular category of diet had the same concentrations of COPCs.

Since the estimated COPC concentrations were calculated using conservative bioaccumulation factors the results are likely to overestimate risk. In addition to the conservative bioaccumulation factors, the assumption of a uniform concentration of COPCs in all species in a prey item category, e.g., invertebrates and mammals, ignores the substantial variability, both in types of prey and expected levels of COPCs.

No modeling of risks due to inorganic constituents was conducted for piscivorous wildlife. Inorganic constituents were not measured in fish or in surface waters. However, barium, copper, thallium, and selenium were considered COPCs for sediment. Barium, copper, and selenium were considered COPCs for wildlife because they exceeded their sediment screening benchmarks and could, theoretically, be accumulated up the food chain from fish into piscivores. Thallium was a COPC only because it was detected in sediment and there are no screening benchmarks for thallium. However, risks from these inorganic constituents were not evaluated for the following three reasons:

1) There is no scientifically valid method for directly relating the concentrations of metals in fish or invertebrates to sediment or surface water concentrations;
2) Both copper and selenium are essential micronutrients that are regulated by both mammals and birds according to their nutritional requirements; and
3) Neither copper nor selenium are COPCs that are known to have been associated with activities at the Site.

Use of Bioaccumulation Factors in Wildlife Modeling

Site-specific measurements of tissue concentrations are the best data to reduce uncertainty in estimating EPCs in dietary components. However, the collection of tissue for all dietary components requires killing animals and is not practical in most ecological risk assessments. Therefore, bioaccumulation factors or models must be applied and a level of uncertainty in estimated concentrations must be accepted. A discussion of this uncertainty is summarized below and provided in detail in Appendix F.

Bioaccumulation factors provide quantitative indicators of the tendency for a chemical to partition into biological organisms relative to the concentrations present in environmental exposure media. The complexity and limited Site-specific understanding of interactions controlling bioavailability of site contaminants lead to uncertainties in estimating the bioaccumulation of these contaminants from environmental media to biological organisms. Because bioaccumulation is generally non-linear, with accumulation decreasing with increasing media concentrations, estimates of prey concentrations based on regression models are less uncertain than estimates of prey concentrations based on constant accumulation factors. In this assessment, regression models were used when available to estimate COPC concentrations in terrestrial plants, soil invertebrates, and small mammals (Bechtel 1998a; Efroymson et al. 2001; USEPA 2005c; Bechtel 1998; Sample et al. 1998; Sample et al. 1999). Constant accumulation factors, used in the absence of appropriate regression models, likely overestimate bioaccumulation at higher media concentrations.

To the extent possible, estimates of the most important contaminants that are components of wildlife diets at the Site, PAHs, were derived directly from measured concentrations in wild fish, or bioassay invertebrates. Since the COPC concentrations were actually measured in fish from the Site the results are unlikely to over or underestimate risk for piscivores. Concentrations of biphenyl, dibenzofuran, and the VOCs identified as COPCs in sediment were estimated based on surrogate BSAFs calculated from the measured concentrations of wild fish and the bioassay invertebrates. Although the use of BSAFs to estimate tissue concentrations introduces more uncertainty than direct tissue measurements, it was determined that the calculated BSAFs were sufficiently conservative relative to BSAFs reported in the literature.

It is likely that BSAFs calculated from laboratory bioaccumulation studies result in an overestimate of risk. The artificial mixing of sediments, the small volume of overlying water in which to reach equilibrium, and the infrequent renewal of this water, assure that laboratory-exposed worms are exposed to greater concentrations of COPCs than occur at the Site. Furthermore, Schuler et al. (2003) have shown that *L. variegatus*, the test organism used in the site-specific bioaccumulation studies, accumulates PAHs to significantly higher concentrations than either *H. azteca* or *C. dilutus* exposed to the same PAH concentrations in both water and sediment. As discussed above, the inability to evaluate the bioavailability of the COPCs in the diet is also likely to lead to overestimation of risk.

Concentrations of invertebrate prey in the wildlife exposure models were calculated based on the geometric means of BSAFs developed for individual PAHs from the bioaccumulation study. At the request of USEPA, concentrations in benthic invertebrates at the Site were estimated based on the UCL_{95} of BSAFs developed from the bioaccumulation study to evaluate the uncertainty in estimating doses to invertivorous wildlife.

Wildlife exposure models based on doses calculated from UCL_{95} BSAFs are presented in Appendix I, Tables I-13 to I-16. The results of the models indicate HQs greater than one for black duck, depending on the NOAEL used as the basis for the HQ, and tree swallow (Table 6-7). Based on the conservative NOAEL for total PAHs and VOCs, doses to black duck and tree swallow based on the UCL_{95} BSAFs resulted in HQs of 6.8 and 11.6, respectively. Based on an alternative NOAEL endpoint, HQs were less than one for black duck and slightly exceeded one for tree swallow. HQs were less than one for the big brown bat using both methods of BSAF calculation and both NOAEL doses.

Table 6-7. Wildlife HQs for Total PAHs and VOCs Based on UCL_{95} BSAFs.

Receptor	NOAEL	
	16.1 mg/kg BW/day	161 mg/kg BW/day
Black Duck	6.8	<1
Tree Swallow	11.6	1.2

6.3.3.4 Uncertainty Associated with Risk Characterization

Hazard Quotients

The hazard quotient method is the simplest and most commonly used method to provide a risk estimate. The major regulatory advantage of the hazard quotient method is that since exposure estimations use the UCL_{95} of abiotic media concentrations, risk is undoubtedly overestimated in most cases. The major potential disadvantage comes from the single estimate of risk that results from a single TRV or benchmark. Since all species have not been tested, and since even different tests with the same organism frequently have different conclusions, it is possible that a given receptor will be more sensitive than the surrogate ROC selected for the TRV or benchmark, and that this will lead to an underestimation of the risk for that particular receptor. As explained above, conservative TRVs and benchmarks as well as EPCs have been used to protect against this possibility.

6.3.3.5 Summary

Because, for most factors considered in this risk assessment conservative estimates or assumptions were made, there is confidence that hazard quotients less than one indicate the potential of adverse effects for that COPC receptor exposure pathway is unlikely.

The results of the risk characterization indicated that there are potentially unacceptable impacts to the benthic macroinvertebrate community in aquatic portions of the Site. Two lines of evidence, bulk sediment chemistry and sediment toxicity testing indicated the potential for impairment at the community level. Effects observed from field surveys of the existing benthic community indicated effects that were less dramatic than those demonstrated in the laboratory toxicity studies, but interpretation of the field survey data is made very difficult by a high degree of variability and lack of comparability between reference and site stations.

However, the fact that hydrocarbons are sporadically released from the Site sediment during some high energy meteorological events or when disturbed by other activity indicates the potential for impact to the benthic community may not have necessarily been fully measured by the benthic community studies conducted to support the RI. While there is no evidence that effects from these releases lead to adverse effects on populations and communities of these receptors inhabiting the waters of Chequamegon Bay, it remains a source of uncertainty. It is possible that the presence of this continuing source of site related contaminants may sporadically impair the healthy functioning of the aquatic community in the Site area.

In addition, if normal lake front activities, i.e, wading, boating etc., were not presently prohibited, the disturbance of sediments and concomitant release of subsurface COPCS would increase. This potentially could lead to greater impacts than were measured during these RI/FS studies.

The BERA concluded that the potential for adverse effects to other ecological receptors was not sufficient to result in significant adverse alterations to populations and communities of ecological receptors.

The following table (Table 7-1) summarizes the results of the BERA.

Table 7-1. Conclusions of the Baseline Ecological Risk Assessment.		
Assessment Endpoint	**Risk Question**	**Conclusion of BERA**
Benthic macroinvertebrate community	Are concentrations of contaminants in the sediments at the Site sufficiently elevated that they cause adverse alterations to the functioning of the benthic macroinvertebrate community?	Based upon two lines of evidence, there are potentially unacceptable impacts to the benthic macroinvertebrate community in aquatic portions of the Site although effects observed from field surveys of the existing benthic community indicated effects that were less dramatic than those demonstrated in the laboratory toxicity studies. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the benthic macroinvertebrate community is exposed to them should be addressed in the Feasibility Study.
Fish community	Are concentrations of contaminants at the Site sufficiently elevated that they cause adverse alterations to the functioning of the fish community?	There is no unacceptable risk to the fish community utilizing the Site. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the fish community is exposed to them should be addressed in the Feasibility Study.
Omnivorous aquatic bird community	Are dietary exposure levels of Site-related contaminants sufficiently elevated to cause adverse alterations to the omnivorous aquatic avian community?	There is no unacceptable risk to the omnivorous aquatic bird community utilizing the Site. However, the presence of contaminants in Site sediment that are sporadically released to the aquatic environment where the omnivorous aquatic bird community is exposed to them should be addressed in the Feasibility Study.
Omnivorous birds	Are dietary exposure levels of site-related contaminants sufficient to cause adverse alterations to the omnivorous avian community?	There is no unacceptable risk to omnivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Insectivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the	There is no unacceptable risk to insectivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.

Table 7-1. Conclusions of the Baseline Ecological Risk Assessment.		
Assessment Endpoint	**Risk Question**	**Conclusion of BERA**
	insectivorous avian community?	
Piscivorous birds	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to individual ospreys or to the piscivorous avian community?	There is no unacceptable risk to piscivorous birds utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Omnivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the omnivorous mammal community?	There is no unacceptable risk to omnivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Insectivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the insectivorous mammal community?	There is no unacceptable risk to insectivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.
Piscivorous mammals	Are dietary exposure levels of Site-related contaminants sufficient to cause adverse alterations to the piscivorous mammal community?	There is no unacceptable risk to piscivorous mammals utilizing the Site. This exposure pathway does not require consideration in the Feasibility Study.

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